148–152° (3 mm.)][17] was added. After the usual work-up the product was fractionated to give 17.8 g. (47.7%) of keto ester; b.p. 195–230° (1 mm.); n_D^{25} 1.4482; d^{25} 0.864. Two carbon-hydrogen analyses indicated that the keto ester was contaminated with ethyl azelate: C, 72.44, 72.54; H, 11.56, 11.65 (calcd. for $C_{21}H_{40}O_3$: C, 74.06; H, 11.87). Cason *et al.*[7] report a 43% yield, b.p. 216–220° (5 mm.).

Ethyl (+)-9-oxo-12-methyloctadecanoate. This ester was prepared using 18.6 g. of (+)-1-bromo-3-methylnonane ($[\alpha]_D^{27}$ +1.15°), 2.02 g. of magnesium, 9.3 g. of cadmium chloride, and 15.9 g. of ω-carbethoxycaprylyl chloride. Distillation gave 14.8 g. (51.9%); b.p. 198–225° (1 mm.); n_D^{25} 1.4481; α_D^{28} +0.10° (homogeneous, 1 dm. tube); $[\alpha]_D^{28}$ +0.11°.

Ethyl (−)-9-oxo-12-methyloctadecanoate. The levorotatory ester was made from 14.4 g. of (−)-1-bromo-3-methylnonane ($[\alpha]_D^{27}$ −1.17°), 1.60 g. of magnesium, 7.16 g. of cadmium chloride, and 12.2 g. of ω-carbethoxycaprylyl chloride. The yield was 9.4 g. (43%); b.p. 191–212° (1 mm.); n_D^{25} 1.4479.

Ethyl DL-*12-methyloctadecanoate* (X). Ethyl DL-9-oxo-12-methyloctadecanoate (17.0 g.), 9.5 g. of potassium hydroxide, 8.5 ml. of 85% hydrazine hydrate, and 85 ml. of diethylene glycol was heated under reflux for 1.5 hr.[6] The mixture was concentrated until the temperature of the solution was 195°, then reflux was continued 4 hr. The reaction mixture was worked up to furnish the acid. The crude acid was esterified with absolute ethanol and sulfuric acid. The ester was ultimately distilled to give 12.3 g. (75.4%) of ethyl DL-12-methyloctadecanoate; b.p. 205–212° (1 mm.); n_D^{25} 1.4425; d^{25} 0.824; sapon. equiv., 319 (calcd. for $C_{21}H_{42}O_2$: 327). Cason *et al.*[7] report b.p. 183–185° (2 mm.), n_D^{25} 1.4463.

Ethyl (+)-12-methyloctadecanoate was prepared by the procedure used above with 14.8 g. of ethyl (+)-9-oxo-12-methyloctadecanoate ($[\alpha]_D^{28}$ −0.10°). After extraction and esterification 10.5 g. (73.1%) of (+)-ester was obtained; b.p. 191–204° (0.5 mm.); n_D^{25} 1.4428; α_D^{28} +0.23° (homogeneous); $[\alpha]_D^{28}$ +0.15°; sapon. equiv., 322 (calcd. for $C_{21}H_{42}O_2$: 327).

Ethyl (−)-12-methyloctadecanoate was prepared by reduction of 9.4 g. (ethyl (−)-9-oxo-12-methyloctadecanoate. After the work-up 5.4 g. (60%) reduced (−)-ester was obtained; b.p. 190–198° (0.5 mm.); n_D^{25} 1.4429; α_D^{30} −0.22° (homogeneous); $[\alpha]_D^{30}$ −0.14°; sapon. equiv., 325 (calcd. for $C_{21}H_{42}O_2$: 327).

DL-*12-Methyloctadecanoic acid* (XI). Ethyl DL-12-methyloctadecanoate (5.2 g.) was heated under reflux for 1 hr. with 3.6 g. of potassium hydroxide in 100 ml. of 95% ethanol. The mixture was diluted with water and extracted with ether. The aqueous phase was acidified with hydrochloric acid and the acid was extracted with benzene. Removal of the solvent and crystallization of the acid from acetone-water mixtures furnished 3.7 g. (78%), m.p. 26–27°, equiv. wt., 299.1 (calcd. for $C_{19}H_{38}O_2$: 298.5). The literature[7] reports m.p. 27.6–28.2°.

The *amide*[2] after 5 crystallizations from methanol-water melted at 84–86°. A mixture containing equal amounts of the (+)- and (−)-amides melted at 76–78°.

The *tribromoanilide*[18] after 5 crystallizations from methanol-water melted at 93–94°. A mixture of equal amounts of (+)- and (−)-forms melted at 91–92°.

(+)-12-Methyloctadecanoic acid was prepared in 92% yield using 5.8 g. of ethyl (+)-12-methyloctadecanoate. Two crystallizations from acetone-water gave 4.9 g. of the (+)-acid; m.p. 37–38°; α_D^{27} +0.09° (homogeneous, 2 dm., tube); equiv. wt., 298.9 (calcd. for $C_{19}H_{38}O_2$: 298.5).

The *amide*[2] after 5 crystallizations melted at 74–75°.

The *tribromoanilide*[18] after 5 crystallizations melted at 89–91°.

(−)-12-Methyloctadecanoic acid was prepared like the other two forms using 5.4 g. of ethyl (−)-12-methyloctadecanoate. Two crystallizations from acetone-water furnished 2.9 g. (59%) of (−)-acid, m.p. 36–37°, α_D^{27} −0.10° (homogeneous, 2 dm. tube); equiv. wt., 299.4 (calcd. for $C_{19}H_{38}O_2$: 298.5).

The *amide*[2] after 5 crystallizations melted at 72–74°.

The *tribromoanilide*[18] melted at 90–92° after 5 crystallizations.

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[17] F. S. Prout and J. Cason, *J. Org. Chem.*, **14**, 132 (1949); *cf.* also H. McKennis, Jr., and V. du Vigneaud, *J. Am. Chem. Soc.*, **68**, 832 (1946).

[18] J. Cason, *J. Am. Chem. Soc.*, **64**, 1106 (1942).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION OF HUMBLE OIL AND REFINING CO.]

Ozonolysis of Norbornylene

ROBERT H. PERRY, JR.

Received November 12, 1958

Ozonolysis of norbornylene in methanol, a "reacting" solvent, gave a mixture of an aldehydic methoxyhydroperoxide and its condensation products, whereas "inert" solvents afforded a polymeric, active oxygen-containing substance tentatively characterized as a polymeric ozonide. The nature and modes of formation of these materials are discussed. Conversion of both products to *cis*-cyclopentane-1,3-dicarboxylic acid was effected in high yield.

In a course of study concerned with the preparation of carboxylic acids from olefins employing ozone as an oxidant, the conversion of norbornylene to cyclopentane-1,3-dicarboxylic acid was investigated. Since the literature does not reveal any reports of ozonolysis studies utilizing this olefin, it was of interest to characterize the intermediate, or active oxygen-containing, products formed prior to oxidative decomposition to the desired acid.

Criegee and co-workers have shown[1] that, in general, the ozonolysis of olefins in hydroxylic or "reacting" solvents gives rise to hydroperoxides

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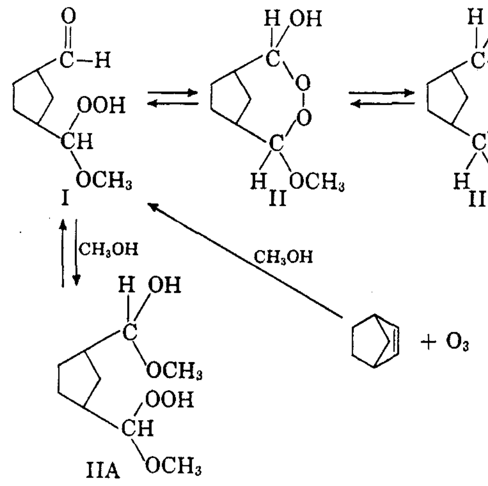
[1] (a) R. Criegee, *Ann.*, **583**, 1 (1953); (b) R. Criegee, G. Blust, and H. Zincke, *Chem. Ber.*, **87**, 766 (1954); (c) R. Criegee, A. Kerchow, and H. Zinke, *Chem. Ber.*, **88**, 1878 (1955); (d) R. Criegee and G. Lohaus, *Chem. Ber.*, **86**, 1 (1953); (e) R. Criegee and G. Lohaus, *Ann.*, **583**, 6 (1953); (f) R. Criegee and G. Wenner, *Ann.*, **564**, 9 (1949); (g) R. Criegee, *Record of Chemical Progress*, **18**, 111 (1957); (h) G. Lohaus, *Chem. Ber.*, **87**, 1708 (1954); (i) P. S. Bailey, *Chem. Ber.*, **88**, 795 (1956); (j) P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956); (k) P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957); (l) P. S. Bailey, *J. Org. Chem.*, **21**, 1335 (1956).

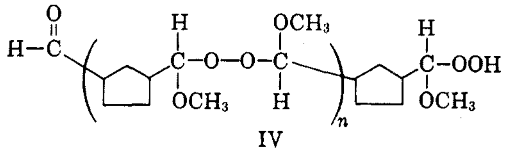
in addition to a carbonyl fragment, whereas aprotic ("inert") solvents allow the formation of ozonides or polymeric peroxides.

It should be noted that some olefins, *e.g.*, 1,2-diphenylindene[2] and 2,3-disubstituted indenones,[2,3] form ozonides in both solvent types. Furthermore, the extent of formation of monomeric ozonides or polymeric peroxidic products, particularly from cyclic olefins, is influenced by substitution in the olefin and the amount of strain in the intermediate.[1c,g] Cyclic olefins which can form a six- or seven-membered ring in addition to the five-membered trioxolane ring give ozonides, whereas polymerization products predominate from cyclic olefins of larger or smaller size.

Discussion and results A. *"Reacting" solvents.* Norbornylene was ozonized in methanol at −78°, and the product appeared to consist largely of an equilibrium mixture of the peroxidic compounds (I, II, and III). It is believed that the aldehydic methoxyhydroperoxide (I) was formed as the initial product, following which intramolecular condensation occurred, in part, to give the labile peracetals (II and III). The possibility exists that some IIA was produced by the other mode of hemiacetal formation, *i.e.*, that involving the aldehyde group and methanol. Although the results did not enable a definite distinction of IIA from the other structures shown, this substance was probably not formed to an appreciable extent, since an aldehyde generally interacts preferentially with a hydroperoxide when the two functions are produced by ozonolysis in alcohols as solvents.[1k] Evidence for the mixture of peroxidic compounds (I–III) as the main product was afforded by qualitative tests, analyses, and conversion to the corresponding dicarboxylic acid and dicarboxaldehyde. Due to the physical nature (viscous oil) and instability of the product, it was not possible to effect a separation of this mixture into analytically pure components by techniques such as distillation, fractional crystallization, or chromatography.



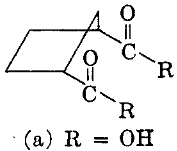
Treatment of the intermediate with sodium iodide resulted in a rapid liberation of iodine followed by a slower reaction. Such behavior would be consistent with the expected lower peroxidic activity of the peracetal forms following the initial, rapid reaction of the hydroperoxide. Treatment with lead tetraacetate brought about oxygen evolution, which is characteristic of hydroperoxides. The material responded weakly to aldehyde tests and decomposed to intractable products when hydrolyzed in the presence of strong acids or bases. Infrared analysis showed strong hydroxyl and carbonyl bands at 3.0μ and 5.85μ, respectively. Elemental and methoxyl group analyses were in accord with the existence of a mixture, with III probably preponderating because of its higher methoxyl content. Active oxygen analyses were low, a result often observed with peroxides. The molecular weight was slightly higher than that calculated for III, indicating the presence of some intermolecular condensation product, probably of the type shown by IV.



IV

The results with norbornylene were similar in many respects to those obtained with cyclohexene in methanol,[1k] except that in the present work the preponderant product was not polymeric. Apparently the intramolecular reaction in the case of cyclohexene was not favored due both to steric limitations in the formation of an eight-membered ring and to the fact that the interacting ends of the molecule are far apart. Moreover, the *cis*-1,3-configuration in I should facilitate the intramolecular reaction.

The active oxygen-containing intermediate was converted to *cis*-cyclopentane-1,3-dicarboxylic acid (Va) in excellent yield (95%) by means of hydrogen peroxide in formic acid. Conversion of the aldehydic methoxyhydroperoxide to suitable derivatives was not successful due to the instability of the material and to the low availability of the aldehyde function under the weakly alkaline conditions of the reactions. Reductive decomposition by means of zinc, or catalytic hydrogenolysis, gave cyclopentanedicarboxaldehyde (Vb).



(a) R = OH
(b) R = H

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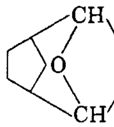
(2) P. S. Bailey, *Chem. Ber.*, **87**, 993 (1954).

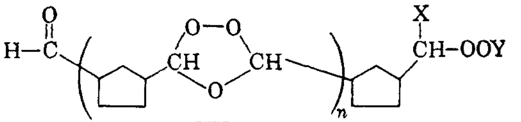
(3) R. Criegee, P. de Bruyn, and G. Lohaus, *Ann.*, **583**, 19 (1953).

B. *"Inert" solvents.* Norbornylene was ozonized in several "inert" solvents and the products isolated in all instances appeared to possess identical properties. At the low temperatures of the reaction (−20° to −78°) the product remained in solution until the mixture was allowed to warm to room temperature, whereupon a highly swollen peroxidic solid precipitated. Purification of this material was difficult because of its insolubility and moderate instability. Similarly, the determination of certain physical properties such as molecular weight and infrared spectrum was not successful. Elemental analysis gave values near those calculated for VI ($C_7H_{10}O_3$):

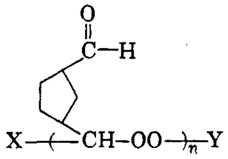


VI

The fact that the properties of the product were those characteristic of polymers precludes VI and suggests VII and VIII as structures for this material. Its ease of hydrolytic decomposition to aldehydic products as well as its oxidation in high yield (95%) to Va favor the polymeric ozonide (VII).

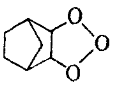


VII

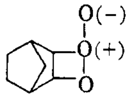


VIII

The soluble substance formed initially during low temperature ozonolysis presumably is unstable and polymerizes as the temperature is increased to near ambient conditions. This intermediate could be the simple ozonide (VI) or one of the forms of a molozonide (IX or X), although the existence of the latter two structural types has not been established. There is no evidence in support of any one structure,



IX



X

but reduction[4] of the low temperature-soluble product should afford *cis*-bicyclo[2.2.1]heptane-2,3-diol from the molozonide, whereas the dialdehyde (Vb) or the corresponding dicarbinol would be the expected product from VI.

Experiments conducted thus far in this regard have been largely without avail due to the lack of suitable reducing agents which are effective at low temperature. Lithium aluminum hydride was partly reactive, but the product was a complicated mixture containing aldehydic function as well as the usual polymeric active oxygen-containing product. Stronger reducing agents are currently being studied, and the nature of the low temperature-soluble substance is being investigated.

EXPERIMENTAL[5]

Norbornylene. This compound was prepared by the method of Joshel and Butz[6] from dicyclopentadiene and ethylene at elevated temperature and pressure. The material used had b.p. 95.0–95.8° (762 mm.), m.p. 44.8–45.2°.

Ozonolysis of norbornylene in methanol. In a typical run 4.0 g. (0.042 mole) of norbornylene in 50 ml. of methanol solution contained in a tubular reactor with a fritted gas inlet were treated at −75° to −20°[7] with an oxygen-ozone stream[8] containing 3 to 4 wt. % ozone. One molar equivalent of ozone was absorbed by the mixture. The methanol was subsequently removed under high vacuum by means of a rotating evaporator maintained at room temperature, and the nonvolatile product was a viscous syrup amounting to 8.4 g. (theory for the monomeric aldehydic methoxy-hydroperoxide is 7.5 g.). Analyses of this product are presented in Table I.

TABLE I

OZONOLYSIS PRODUCT FROM METHANOL

	Calculated[a] for			
Analysis, %	III	IIA	I, II	Found[b]
C	57.10	52.41	55.16	54.73
H	8.53	8.80	8.10	8.39
Active oxygen	8.50	7.77	9.20	7.16-
			—	6.73
Methoxyl	32.80	30.09	17.82	33.16
Molecular weight[c]				
Immediately	189	206	174	212
After 21 days				225

Infrared analysis (film): Strong —OH absorption band at 3.0μ; strong carbonyl band at 5.85μ.

[a] $C_9H_{16}O_4$ (III); $C_9H_{18}O_5$ (IIA); $C_8H_{14}O_4$ (I, II). [b] Elemental and methoxyl group analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [c] Determined cryoscopically in benzene at several concentrations; M. W. obtained from extrapolated values.

The sirup reacted with sodium iodide and liberated oxygen with lead tetraacetate. With the former reagent the iodine liberated in the initial rapid reaction was removed by sodium thiosulfate solution, but the iodine color repeatedly returned, although more slowly, even after several successive treatments with thiosulfate. No reaction occurred in the

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(4) Suggestion by Prof. W. von E. Doering.

(5) Melting points are uncorrected. Infrared spectra were determined either with a Baird Model B or a Perkin-Elmer Model 21 infrared spectrophotometer fitted with a sodium chloride prism.

(6) L. M. Joshel and L. W. Butz, *J. Am. Chem. Soc.*, **63**, 3350 (1941).

(7) Reactions conducted at room temperature or slightly below resulted in appreciable attack by ozone on methanol, thus giving indistinct end points in the ozone-olefin reaction.

(8) Produced by a laboratory ozonator, Model T-23, manufactured by the Welsbach Corp., Philadelphia, Pa.

cold with water, mineral acids and bases, or hydrogen peroxide. Decomposition of the product occurred when these mixtures were heated. The sirup responded mildly to Tollen's and Fuchsin's tests.

Oxidation of peroxidic product (methanol) to cis-cyclopentane-1,3-dicarboxylic acid. The sirup remaining from the evaporated methanolic solution was dissolved in 35 ml. of 90% formic acid, and 20 g. (0.18 mole) of 30% hydrogen peroxide was added. The solution was warmed to approximately 52°, and a strongly exothermic reaction ensued causing refluxing for 15–20 min. Excess peroxide was destroyed by heating 1 hr. longer. The solution was evaporated to dryness on a rotating evaporator, leaving a fine white crystalline residue; m.p. 110–115°. Recrystallization from cold water and recovery from mother liquors afforded 6.5 g. (95% yield) of pure *cis*-cyclopentane-1,3-dicarboxylic acid; m.p. 120.5–121.0°; lit.,[9] 121°. Neut. equiv.: calcd., 79.1. Found, 79.4.

Anal. Calcd. for $C_7H_{10}O_4$: C, 52.98; H, 6.18. Found: C, 53.17; H, 6.38.

Attempted preparation of derivatives of ozonolysis intermediate (methanol). Attempts were made to prepare aldehyde derivatives from the active oxygen intermediate before and after isolation from methanol. Hydroxylamine hydrochloride with pyridine or sodium acetate solutions, semicarbazide hydrochloride under similar conditions and 2,4-dinitrophenylhydrazine in acidified ethanol gave intractable mixtures.

Reductive decomposition of peroxidic product (methanol) to cyclopentane-1,3-dicarboxaldehyde. The alcoholic solution was reduced by catalytic hydrogenolysis employing platinum oxide or by means of zinc dust and water. In the latter instance the methanolic solution (0.1 mole) was added dropwise to a stirred mixture of zinc dust (0.1 mole) and water (100 ml.), during which time the temperature rose to 54°. The mixture was heated to 85° for 2 hr., filtered, the filtrate saturated with salt, and extracted continuously with ether for 24 hr. The material boiling at 70–75°/1 mm. was collected; lit.[10] b.p. 74–75°/1.5 mm. The crude product was converted to the *bis*-2,4-dinitrophenylhydrazone using an acetic acid solution of 2,4-dinitrophenylhydrazine rather than mineral acid; m.p. 225–226°.

Anal. Calcd. for $C_{19}H_{18}N_8O_8$: C, 46.91; H, 3.70; N, 23.04. Found: C, 46.50; H, 3.71; N, 22.75.

Ozonolysis in "inert" solvents. Reactions in these media (ethyl acetate, carbon tetrachloride, chloroform, tetrahydrofuran, etc.) were performed in a stirred reactor provided with gas inlet tube (without fritted tip) in a manner similar to that described previously. The temperatures normally were maintained at −75° or as low as the solvent would allow. Ozone was rapidly absorbed until 0.90 to 0.95 molar equivalent had been added, following which absorption was incomplete. The solvents allowing reactions at −75° to about −40° gave essentially clear solutions at the end of the ozonolysis period. Normally, as the mixture warmed to near room temperature the solution became turbid, and after 2–3 hr. at room temperature, complete precipitation of a highly swollen "gel" occurred. The solvent was removed from the solid (*S*) by suction filtration and freeze drying, the last traces being removed very slowly. A small amount of gummy residue (*G*), *ca.* 5% or less of the product, remained on evaporation of the filtrate. This material exhibited similar chemical behavior to *S*. It swelled with partial dissolution in the original solvent. Substance *G* from analyses and properties was suspected as being a lower molecular weight polymer, similar otherwise to the main product. Both *S* and *G* were insensitive to shock but burned violently in an open flame. Substance *S* appeared to be stable in a vacuum desiccator for several days but decomposed to gummy aldehydic products on standing in contact with air at room temperature over the same period.

Due to the insolubility of *S* and *G* in solvents other than those which caused decomposition [the latter including pyridine, dimethylformamide, methanol (hot) and acetic acid (hot)], the preparation of an analytically pure species was difficult (analyses, Table II). Active oxygen analyses were lower than those calculated for VI, a result which has often been observed[11] with ozonides and other peroxidic compounds, due partly to their tendency to undergo the "acid rearrangement." No reaction occurred in the cold with water or hydrogen peroxide, whereas decomposition occurred when these mixtures were heated. Mineral acids and bases caused moderately rapid decomposition.

TABLE II

OZONOLYSIS PRODUCT FROM INERT SOLVENTS

[M.p. (*S*) 95–105° (dec.)]

Analysis, %	Calculated[a]	Found[b] Precipitate (*S*)	Gum (*G*)
C	59.15	58.30	57.63
H	7.04	7.48	7.31
O	33.80	34.31	—
Active oxygen	11.3	5.22[c] 5.70[d]	4.38 4.34

[a] For $C_7H_{10}O_3$ (VI). [b] See footnote *b*, Table I. [c] Allowed to stand 1 hr. at room temperature with sodium iodide and glacial acetic acid followed by 1 hr. reflux; less blank. [d] Allowed to stand 2 hr. at room temperature; less blank.

Infrared analysis was attempted in KBr and mulls with decomposition occurring during each preparation. Infrared analyses were made on solutions removed from the reactor during ozonolyses in methyl chloroform, since precipitation of product in this solvent was very slow. These mixtures exhibited an increasingly intense carbonyl absorption at 5.85μ, but this was suspected as being due to the presence of decomposition products.[12]

Oxidation of peroxidic product (inert solvents) to cis-cyclopentane-1,3-dicarboxylic acid. This reaction was conducted in a manner similar to that with the product from methanol. The yield was 95% of high purity product.

Attempted reduction of low temperature-soluble "ozonide." Norbornylene was ozonized at −55° in carefully dried tetrahydrofuran. An excess of lithium aluminum hydride solution in tetrahydrofuran was slowly added to the completely ozonized mixture containing the dissolved product, and an exothermic reaction occurred accompanied by copious precipitation of white solid. The mixture was stirred at −50° for 2 hr., then allowed to warm to room temperature, and the hydride and the complex were destroyed with water and dilute sulfuric acid, respectively. In addition to the normal peroxidic product (*S*), an oil was obtained which contained hydroxyl and aldehyde function. Attempts to separate the components in this mixture were not successful.

Other reducing agents including ferrous sulfate, sodium sulfite and catalytic hydrogenolysis were unreactive at −40°.

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(9) W. H. Perkin and H. A. Scarborough, *J. Chem. Soc.*, **119**, 1405 (1921).

(10) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 2824 (1957).

(11) R. Criegee, *Fortsch. Chem. Forsch.*, **1**, 508 (1950).

(12) E. Briner and E. Dallwigk, *Helv. Chim. Acta*, **39**, 1446 (1956).

Acknowledgments. The author wishes to thank the Humble Oil and Refining Co. for permission to publish this work. The helpful counsel and advice of Professor Philip S. Bailey is especially appreciated. Thanks are due Mr. Harold Kail for assistance in conducting the experimental work and Dr. B. H. Johnson and Miss Marjorie Walker for certain analyses.

BAYTOWN, TEX.

[CONTRIBUTION FROM MELLON INSTITUTE]

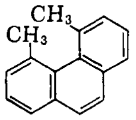
Ultraviolet Spectra of Benzo[c]phenanthrenes

A. WILLIAM JOHNSON

Received November 17, 1958

1,8,9-Naphthanthracene (VI) has been prepared by reduction of the ketone (VII). A second hydrocarbon, 2,3-trimethylenepyrene (VIII), was also isolated. Comparison of the ultraviolet spectra of VI with those of other benzo[c]phenanthrenes provided evidence for intramolecular overcrowding between the C_1 and C_{12} hydrogens in benzo[c]phenanthrene.

Jones[1] has attempted to correlate the differences in fine structure observed in the ultraviolet spectra of many polynuclear aromatic hydrocarbons. The "Fine Structure (Fs) Effect," which was an outgrowth of these correlations, referred to an increase of fine structure produced by the fusion of alicyclic rings to an aromatic nucleus.[2] However, Jones and, more recently, Friedel[3] both pointed out a large number of exceptions to the general rule. The latter indicated that the Fs effect, as originally outlined by Jones, was not generally applicable to polynuclear hydrocarbons and in its place offered a tripartite correlation of the spectra of aromatic hydrocarbons containing fused alicyclic rings.



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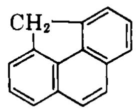
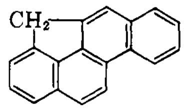
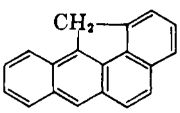


II

The ultraviolet spectrum of 4,5-dimethylphenanthrene (I) shows a marked decrease in fine structure (band splitting) when compared with the spectrum of 4,5-methylenephenanthrene (II)[2a] (Fig. 1). However, the parent hydrocarbon, phenanthrene, exhibits a spectrum very similar in detail to that of II. Analogous relationships are found in the chrysene[4] and 1,2-benzanthracene[5] series. 4,5-Methylenechrysene (III) and chrysene exhibit more fine structure in their spectra than does 4,5-dimethylchrysene. Similarly, both 1′,9-methylene-1,2-benzanthracene (IV) and 1,2-benzanthracene show more band splitting than 1′,9-dimethyl-



III



IV

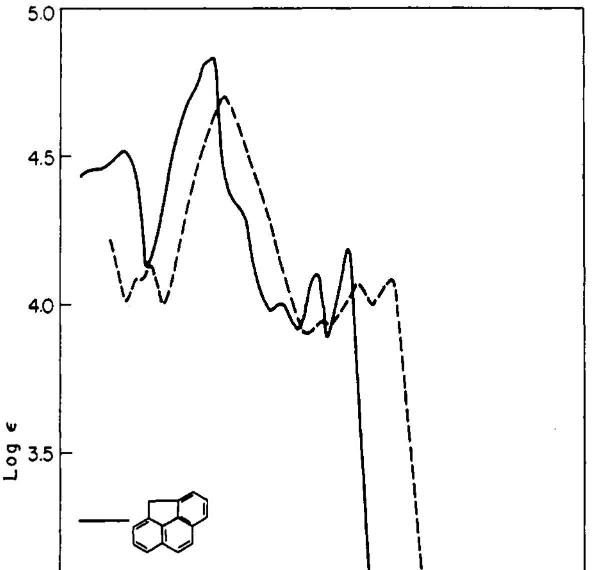


Fig. 1. 4,5-Dimethylphenanthrene (Ref. 2 (b), Spectrum No. 352) (I). 4,5-Methylenephenanthrene (Ref. 2 (b), Spectrum No. 363) (II)

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[1] R. N. Jones, *J. Am. Chem. Soc.*, **67,** 2127 (1945).

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[4] R. N. Jones, *J. Am. Chem. Soc.*, **63,** 313 (1941).

[5] R. N. Jones, *J. Am. Chem. Soc.*, **62,** 148 (1940).