

The Determination of Double-Bond Character in Cyclic Systems. VI.¹ Anthracene. Evidence for Benzenoid Terminal Rings²

John L. Ferrari, I. Moyer Hunsberger,³ and H. S. Gutowsky

Contribution from the Departments of Chemistry, Fordham University, New York, New York, University of Massachusetts, Amherst, Massachusetts, and University of Illinois, Urbana, Illinois. Received November 19, 1964

Extension to anthracene of the infrared method for determination of bond order has led to the conclusion that the end rings of anthracene are much more benzenoid than previously supposed and that "long-bonded" Dewar and/or corresponding ionic structures contribute importantly to the structure of the middle ring. Since 2-hydroxy-1-anthraldehyde, the corresponding methyl ketone, and their 2,3-isomers all exhibit $\Delta\nu_{C=O}$ values¹ of approximately the same magnitude as those earlier found for analogous derivatives of benzene, indan, *o*-xylene, and tetrahydronaphthalene, both the 1,2- and 2,3-bonds of anthracene must exhibit close to 50% double bond character, a conclusion contrary to theoretical expectations. An electronic effect peculiar to linear acenes is postulated to explain the small, but consistent, amount by which the $\Delta\nu_{C=O}$ values for both the 1,2- and 2,3-derivatives of anthracene exceed the corresponding values for the analogous derivatives of the above-mentioned benzenoid hydrocarbons.

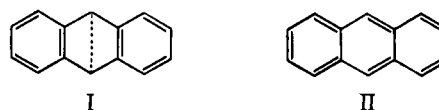
Introduction

The infrared method for the determination of bond orders in aromatic systems has been described previously.^{1a-d} The present work extends this experimental method to an investigation of the 1,2- and 2,3-bonds of anthracene.

The calculated bond orders⁴ of corresponding bonds (A and B) in anthracene, benzene, and naphthalene (obtained by the Pauling, valence bond (VB), and molecular orbital (MO) methods) are given in Table I. While a comparison of the absolute bond orders obtained for a given bond by the three methods has no significance, one instance of qualitative disagreement between the Pauling and MO values on the one hand and the VB values on the other has received insufficient recognition. Thus, the VB treatment assigns bond A of anthracene a lower bond order than bond A of naphthalene, and a higher bond order to bond B of anthracene than to bond B of

naphthalene. Both the MO and Pauling methods ascribe a higher bond order to bond A and a lower order to bond B of anthracene as compared with the corresponding bonds in naphthalene (see Table I). Evidence presented in the present paper is in closer agreement with the VB bond orders than with the MO or Pauling values.

Because of the formidable difficulties involved, no rigorous bond-order calculations for anthracene have been performed. Simpler VB treatments, in which atomic orbitals are assumed to be mutually orthogonal and ionic structures are ignored, are sometimes justified. However, in complex systems these methods may lead to oversimplifications. For example, while detailed (but not fully rigorous) calculations on anthracene lead to the conclusion that structure I has greater weight than the more "stable" structure II, Wheland⁵ indicates that



this result probably is incorrect; analogy with work performed on simpler systems (butadiene and benzene) is said to offer some justification for ignoring structures like I (and corresponding ionic structures). However, results of the present work support the more detailed calculations and the work of the Pullmans,⁶ who stress the importance of contributing structures such as I in calculations on acenes.

This paper presents the results of an experimental study of the bond orders of anthracene and a comparison of these results with our previous work on benzene, naphthalene, tetrahydronaphthalene, indan, and *o*-xylene. The existence of a small electronic effect on the carbonyl stretching frequency (presumably peculiar to acenes) also is described. These results indicate that bond A of anthracene has, at most, slightly more than 50% double bond character (DBC) and bond B slightly less than 50% DBC. Thus, the implication is clear that Dewar, ionic, or similar structures contribute importantly to the structure of the central ring and that the terminal rings are considerably more benzenoid than presently supposed. Our results permit the further conclusion that the terminal rings of anthracene are considerably more benzenoid than the component rings of naphthalene.

Discussion

Synthetic Work. All of the monosubstituted anthracenes (III and IV) required for this study are

(5) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 23, 639, 654.

(6) Ref. 4, p. 32 ff.


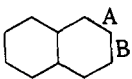
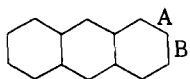
(1) (a) I. M. Hunsberger, *J. Am. Chem. Soc.*, **72**, 5626 (1950); (b) I. M. Hunsberger, R. Ketcham, and H. S. Gutowsky, *ibid.*, **74**, 4839 (1952); (c) I. M. Hunsberger, D. Lednicer, H. S. Gutowsky, D. L. Bunker, and P. Taussig, *ibid.*, **77**, 2466 (1955); (d) I. M. Hunsberger, H. S. Gutowsky, W. Powell, L. Morin, and V. Bandurco, *ibid.*, **80**, 3294 (1958); (e) A. L. Porte, H. S. Gutowsky, and I. M. Hunsberger, *ibid.*, **82**, 5057 (1960).

(2) This paper is taken in part from the Ph.D. Dissertation of J. L. F., Fordham University, 1963. Parts of the work reported herein were presented at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1959, Abstracts of Papers, p. 21P. See also J. L. Ferrari and I. M. Hunsberger, *J. Org. Chem.*, **25**, 485 (1960).

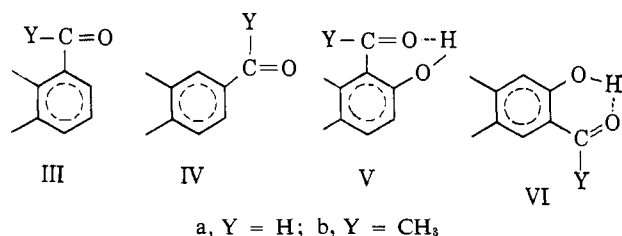
(3) Department of Chemistry, University of Massachusetts, Amherst, Mass. To whom all inquiries should be addressed.

(4) Taken from B. Pullman and A. Pullman, "Progress in Organic Chemistry," Vol. 4, J. W. Cook, Ed., Butterworth and Co. (Publishers), Ltd., 1958, pp. 34, 38.

Table I. Calculated Bond Orders

							
	A and B	A	B	A-B	A	B	A-B
Pauling	0.500	0.667	0.333	0.334	0.750	0.250	0.500
VB	0.463	0.557	0.367	0.190	0.452	0.387	0.065
MO	0.667	0.725	0.603	0.122	0.738	0.586	0.152

known^{7,8} However, the aldehydes IIIa⁹ and IVa were prepared from the corresponding methyl ketones IIIb and IVb via a mild oxidation procedure,¹⁰ and IVa also was prepared by application of a McFadyen-Stevens reaction to 2-anthrylbenzenesulfonylhydrazide.



Of the disubstituted anthracenes, only VIa is a new compound, the rest having been prepared recently.^{11,12} However, Jain and Seshadri¹¹ reported that the high temperature Fries rearrangement (145° for 1.5 hr., no solvent) of 2-anthryl acetate produced an 83% yield of Vb, m.p. 218–219° dec., whose structural assignment rested on its transformation to alizarin. Our repeated attempts to duplicate their high yields produced yields of only 3–13%. However, under somewhat different conditions (0.5 hr. at 120–130°) we obtained, in addition to the high-melting product, a lower melting isomer (m.p. 116–117°) in approximately the same yield. The yield of the latter product was raised to 58% if the reaction was performed at room temperature in nitrobenzene. Shah and Sethna¹² have reported the lower melting isomer (m.p. 112–113°) in unspecified, low yield from the reaction in nitrobenzene at room temperature; their rigorous proof of structure (independently employed by us) established that the lower melting isomer really had structure Vb. They apparently did not obtain the higher melting isomer. Mixture melting points and comparison of the infrared spectra of the methyl ether and the acetate of Vb with the corresponding derivatives of the higher melting compound showed that they were different. Our assignment of structure VIb to the higher melting isomer was based on the presence of a strong intramolecular hydrogen bond, as demonstrated by the infrared spectrum in dilute solution.

Reaction of 2-methoxyanthracene with N-methylformanilide and phosphorus oxychloride produced a difficultly separable mixture (70% yield) of 2-methoxy-1-anthraldehyde (VIIa) and 3-methoxy-2-anthraldehyde

(VIIIa) in approximately equal amounts. Demethylation of VIIa and VIIIa produced, respectively, Va and VIa. The structure of VIIa followed from its oxidation to 2-methoxyanthraquinone 1-carboxylic acid (IX), identical with an authentic sample¹³; also, the demethylated product (Va) was identical with the product of a Gattermann reaction on 2-anthrol.¹¹ The structure of VIIIa was demonstrated by the fact that the infrared spectrum of its demethylation product (VIa) in dilute solution showed the presence of a strong intramolecular hydrogen bond. Scheme I contains a summary of the above reactions and of those to be described below.

Application of the haloform reaction to the methyl ether (VIIb) of Vb produced IX, plus what most probably was 2-methoxy-1-anthryl trichloromethyl ketone (X), which was not obtained in sufficient purity to permit a satisfactory combustion analysis. However, alkaline hydrolysis of X yielded 2-methoxyanthracene and 2-methoxy-1-anthroic acid (XI), m.p. 204–205°. It is of parenthetical interest to note that these results differ from those reported¹⁴ from application of the haloform reaction to the isomeric methyl 1-methoxy-2-anthryl ketone. In the latter case, methyl 1-methoxy-2-anthraquinonyl ketone was the primary oxidation product, which, when subjected again to the haloform reaction, produced 1-methoxyanthraquinone 2-carboxylic acid.¹⁵

Prior to our knowledge of Shah and Sethna's work,¹² Va and Vb had been shown to have the same orientation. Thus, permanganate oxidation¹⁰ of VIIa produced, in addition to IX, 2-methoxy-1-anthroic acid (XI), identical with the hydrolysis product of X. Chromic acid oxidation of VIIIa produced only 2-methoxyanthraquinone, while permanganate oxidation¹⁰ produced what most probably was 3-methoxy-2-anthroic acid (XII), m.p. 162–163°.

Infrared Work. Previous work¹ has shown that the strength of the intramolecular hydrogen bond in *o*-hydroxy derivatives of aromatic aldehydes, aryl methyl ketones, and aromatic esters varies with the bond order of the ring bond between the carbon atoms bearing the hydroxyl- and carbonyl-containing substituents. The strength of these intramolecular hydrogen bonds is measured by the shift, $\Delta\nu_{C=O}$, to lower frequency of the C=O absorption band in going from the aromatic aldehyde, aryl methyl ketone, or aromatic ester to the *o*-

(7) Apparently the first preparation of IIIa and IVa appeared while the present work was in progress: P. H. Gore, *J. Chem. Soc.*, 1616 (1959).

(8) E. G. E. Hawkins, *ibid.*, 3858 (1957).

(9) For a recent preparation of IIIa see C. Culbertson and R. Pettit, *J. Am. Chem. Soc.*, **85**, 741 (1963).

(10) J. Cymerman-Craig, J. W. Loder, and B. Moore, *Australian J. Chem.*, **9**, 222 (1956).

(11) A. C. Jain and T. R. Seshadri, *J. Sci. Ind. Res. (India)*, **15B**, 63 (1956).

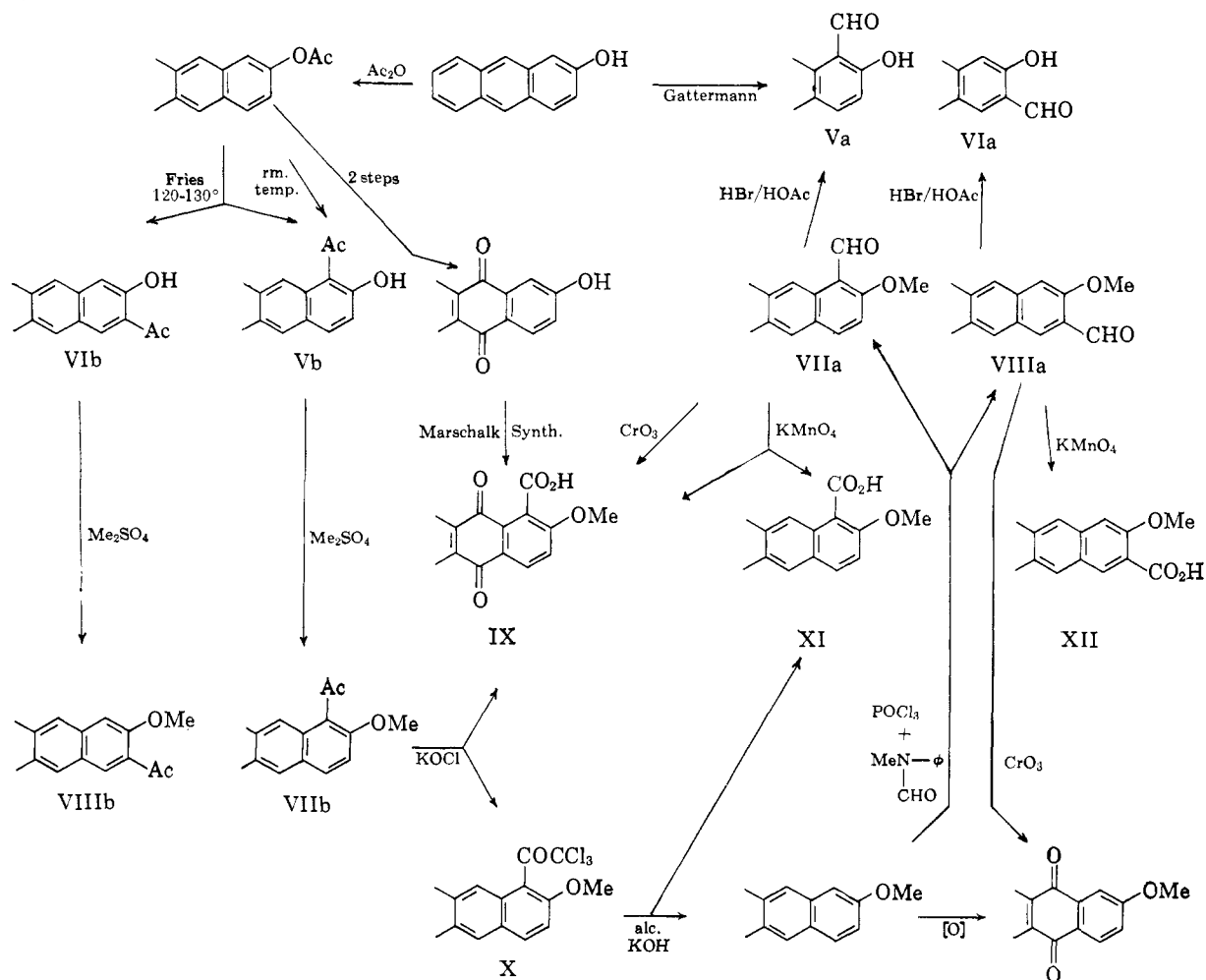
(12) N. H. Shah and S. Sethna, *J. Org. Chem.*, **24**, 1783 (1959).

(13) C. Marschalk, *Bull. soc. chim. France*, [5] **6**, 655 (1939).

(14) S. S. Lele, N. H. Shah, and S. Sethna, *J. Org. Chem.*, **21**, 1293 (1956).

(15) A possible explanation of these results is that the bulky acetyl group hinders oxidation at the 9-*meso* position (which is conjugated with the 2-methoxyl group) and itself reacts preferentially when in the 1-position; when in the 2-position, the acetyl group is distant from the activated 10-position (which is conjugated with the 1-methoxyl group), and oxidation occurs preferentially at the *meso* positions.

Scheme I



hydroxy derivative thereof. Such $\Delta\nu_{C=O}$ terms have characteristic magnitudes for each ring bond in an arene. Furthermore, a linear relationship has been observed between $\Delta\nu_{C=O}$ and bond order for various ring bonds in benzene, naphthalene, phenanthrene,^{1b} and pyridine.¹⁶ If the *o*-hydroxycarbonyl compound also

Table II. C=O Frequencies and $\Delta\nu_{C=O}$ Values for Anthracene Derivatives in 0.02 *m* Carbon Tetrachloride

Compd.	C=O, cm. ⁻¹	$\Delta\nu_{C=O}$, cm. ⁻¹
1-Anthryl methyl ketone (IIIb)	1682	
1-Anthraldehyde (IIIa)	1691	
2-Anthryl methyl ketone (IVb)	1684	
2-Anthraldehyde (IVa)	1691	
2-Hydroxy-1-anthryl methyl ketone (Vb)	1624	58
2-Hydroxy-1-anthraldehyde (Va)	1639	52
3-Hydroxy-2-anthryl methyl ketone (VIb) ^a	1635	49
3-Hydroxy-2-anthraldehyde (VIa) ^b	1641	50

^a The solubility of this compound was so low in carbon tetrachloride that its spectrum was determined in 0.005 *m* chloroform.
^b Also exhibited bands at 1672 (medium) and 1738 cm.⁻¹ (very strong).

bears a methyl (or methylene) group *ortho* to the carbonyl group, the methyl (or methylene) group produces a small, but measureable, increase in the observed

$\Delta\nu_{C=O}$. This phenomenon has been called "steric facilitation of chelation."^{1d}

In Table II are recorded the carbonyl absorption frequencies of compounds III–VI in dilute carbon tetrachloride, as well as the $\Delta\nu_{C=O}$ values for V and VI.

Table III compares the $\Delta\nu_{C=O}$ values for V and VI with those determined previously¹ for the corresponding derivatives of benzene, naphthalene, indan, *o*-xylene, and tetrahydronaphthalene. Throughout this paper, bond A corresponds to the 1,2-bond of anthracene and of naphthalene, the 3,4-bond of *o*-xylene, the 4,5-bond of indan, and the 5,6-bond of tetrahydronaphthalene, while bond B corresponds to the 2,3-bond of anthracene and of naphthalene, the 4,5-bond of *o*-xylene, the 5,6-bond of indan, and the 6,7-bond of tetrahydronaphthalene.¹⁷

The average $\Delta\nu_{C=O}$ values for both bonds A and B of anthracene are of the same order as (although slightly larger than) those for the corresponding bonds of indan, *o*-xylene, and tetrahydronaphthalene. The $\Delta\nu_{C=O}$ (A–B) value for anthracene (5 cm.⁻¹) is of the same order as (although slightly smaller than) the corresponding values for the other three hydrocarbons listed. Hence, the bond orders of bonds A and B in anthracene presumably are similar to the bond orders of the corresponding bonds of *o*-xylene, indan, and tetrahydro-

(16) D. Heinert and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 3933 (1959).

(17) In this paper, only the $\Delta\nu_{C=O}$ values previously obtained for the aldehydes and methyl ketones are considered, since the ester derivatives of anthracene were not studied. However, Heinert and Martell¹⁶ demonstrated that the $\Delta\nu_{C=O}$ values of the aldehydes alone sufficed for a semiquantitative differentiation of bond orders in pyridine.

Table III. $\Delta\nu_{C=O}$ Values in Cm.^{-1} ^a

Y	Benzene	Naphthalene	Anthracene	Indan	<i>o</i> -Xylene	Tetrahydronaphthalene
H	38	51	52	48	50	50
CH ₃	45	57	58	51	49	54
Average	42	54	55	50	50	52
H	38	27	50	43	37	46
CH ₃	45	28	49	40	41	39
Average	42	28	50	42	39	43
$\Delta\nu_{C=O}(A-B)^b$	0	26	5	8	11	9

^a The $\Delta\nu_{C=O}$ values for phenanthrene are not included, since only its 9,10-bond was studied. ^b This term equals the value (in cm.^{-1}) obtained by subtracting the average $\Delta\nu_{C=O}$ value for bond B from the average $\Delta\nu_{C=O}$ value for bond A.

naphthalene. Most noteworthy is the fact that the $\Delta\nu_{C=O}(A-B)$ value for anthracene (5 cm.^{-1}) is *much less than the corresponding value for naphthalene* (26 cm.^{-1})! Presently favored theoretical considerations (MO and Pauling bond orders) lead one to expect that the $\Delta\nu_{C=O}(A-B)$ value for anthracene would be even larger than for naphthalene, since the difference in the MO or Pauling bond orders for bonds A and B is larger for anthracene than for naphthalene (see Table I). On the other hand, the presently less favored VB bond orders exhibit qualitative consistency with our results, in that the difference in VB bond orders for bonds A and B of anthracene is less than for naphthalene (see Table I).

Three factors conceivably could influence the $\Delta\nu_{C=O}$ values for bond A: (a) the bond order of that bond, (b) electronic "substituent" effects, and (c) steric effects.^{1d,18,19} Any steric effect on the substituents around bond B in any of the compounds listed in Table III certainly is negligible. Since the observed $\Delta\nu_{C=O}$ values for the various bonds in benzene, naphthalene, pyridine, and phenanthrene bear an equally precise linear relationship to each of the above-mentioned calculated bond orders (MO, VB, and Pauling), it seems apparent that any differences in the substituent effects in these systems are either too small to be significant or are self-compensating (as might be expected from the basic rationale of the method^{1a}). In other words, it seems likely that the type and degree of conjugation of the rest of the aromatic molecule with the carbon-to-carbon ring bonds under consideration are nearly the same in all of these compounds (except the anthracenes).

The consistently higher average $\Delta\nu_{C=O}$ values for bond A (as compared with bond B) in indan, *o*-xylene, and tetrahydronaphthalene have been attributed to a steric effect whose magnitude is reflected by the magnitude of $\Delta\nu_{C=O}(A-B)$.^{1d} The small $\Delta\nu_{C=O}(A-B)$ value

(5 cm.^{-1}) observed for anthracene may indicate that bond A has a slightly greater bond order than bond B or that the *meso* hydrogen of anthracene exerts a small steric effect on the carbonyl group in the 1-position.²⁰ It seems probable that both of these factors may be operative. In the unlikely event that the $\Delta\nu_{C=O}(A-B)$ value of 5 cm.^{-1} reflects solely a difference in DBC, bonds A and B in anthracene would correspond, respectively, to about 53% and 47% DBC.²¹

Since *both* bonds A and B in anthracene exhibit larger $\Delta\nu_{C=O}$ values than the corresponding bonds in any of the other arenes listed in Table III, an appreciable electronic substituent effect appears to be operating *only* in anthracene. Since the $\Delta\nu_{C=O}$ values for B-type bonds are free of components arising from steric effects, the magnitude of the electronic substituent effect in anthracene is reflected by the difference (8.5 cm.^{-1})²² between the average $\Delta\nu_{C=O}$ value for bond B in anthracene (50 cm.^{-1}) and the corresponding values for bonds B in indan (42 cm.^{-1}), *o*-xylene (39 cm.^{-1}), tetrahydronaphthalene (43 cm.^{-1}), and benzene (42 cm.^{-1}) (see Table III). This approximation obviously does not take into consideration any (presumably small) differences in DBC in the B-type bonds of the pertinent arenes.

A further argument in favor of the existence of an appreciable electronic substituent effect only in anthracene may be understood by consideration of the $\nu_{C=O}$ values listed in Table IV. It is immediately apparent that the anthraldehydes and the anthryl methyl ketones absorb at lower frequencies than corresponding derivatives of all the other arenes listed, thus indicating a greater degree of single bond character for the carbon-to-oxygen bond in the anthracene derivatives. This, in turn, may be attributed to a greater degree of conjugation between the carbonyl group and the aromatic moiety in anthracene than is the case with the other compounds listed. That this difference is one of kind rather than degree is suggested by the fact that the $\nu_{C=O}$ values of the anthracene derivatives are even lower than those of the 9-substituted phenanthrenes.

The experimental results described above would seem to force the conclusion that Dewar-type structures (such as I) and/or corresponding ionic structures and, perhaps, even diradical structures contribute impor-

(20) Any electronic substituent effect of the rest of the anthracene molecule is assumed to affect bond A in the same manner and to the same extent as bond B.

(21) These values were estimated by assuming 50% DBC for the bonds in benzene, and, since $\Delta\nu_{C=O}$ is linearly related to DBC, the simple relation ($5:42 = X:50$) provides ~6% as the difference in DBC between bonds A and B of anthracene. If one makes the eminently reasonable assumption that the sum of the DBC values of the *aromatic* bonds A and B of anthracene is 100%, simple arithmetic provides 53% DBC for bond A and 47% for bond B. These values are in closest agreement with those given by the VB method. That this is not an apologia for the VB method is seen by a similar examination of bonds A and B of naphthalene. In this case, the Pauling bond orders provide the closest agreement with the experimental $\Delta\nu_{C=O}$ values. Our present results for anthracene are in closest agreement with the VB theory, not because it is superior to other theories, but because this method gives consideration to long-bonded structures, which apparently are very important *only* in anthracene. Thus, the VB method does not give good results for naphthalene, in which long-bonded structures are not important. Each theory, therefore, is only as valid as the assumptions made in its application, and it is incorrect to favor one over another since each has characteristic merits and faults in specific applications.

(22) Obtained from the calculation $50 - \frac{42 + 42 + 39 + 43}{4} = 8.5$ (see Table II).

(18) N. Fuson, M. L. Josien, and E. M. Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954).

(19) R. E. Kagarise, *ibid.*, **77**, 1377 (1955).

Table IV. $\nu_{C=O}$ Values in Cm.^{-1}

Substitution	Benzene	Naphthalene	Phenanthrene ^a	Anthracene	Indan	<i>o</i> -Xylene	Tetrahydronaphthalene
1-CHO	1708	1700	1698	1691	1703	1700	1699
2-CHO		1702		1691	1700	1699	1706
1-COCH ₃	1693	1685	1685	1682	1686	1691	1685
2-COCH ₃		1685		1684	1686	1690	1688

^a These values are for 9-substituted carbonyl derivatives of phenanthrene.

tantly to the ground-state structure of anthracene. Such a conclusion would account for the markedly greater (than previously supposed) benzenoid character of the terminal rings and the unusual degree of conjugation between functional groups and the aromatic residue; it also is consistent with virtually all known properties of anthracene.²³ For example, as the first "true" member of the linear "acenes," anthracene long ago was recognized to exhibit chemical reactivity unusual with respect to other aromatic systems. Indeed, the early, common practice of representing anthracene with a "long bond" connecting the 9,10-position (in use as late as the 1920's) was an attempt to illustrate this unusual reactivity and was abandoned mainly because of disagreement with bond lengths determined by X-ray methods and because of the reasonable assumption that the distance between the *meso* carbons would be too long to permit the existence of a covalent bond in a planar molecule. However, a spectacular illustration of the greater reactivity of acenes as compared with their angular counterparts is afforded by a comparison of the highly reactive hexacene²⁴ with the more "aromatic," but isomeric, hexahelicene.²⁵

While chemical reactions, in themselves, are of little value in studies concerning bond order, it is important that bond orders be able to provide a valid basis for explanations of chemical reactivity. For example, on the basis of X-ray bond lengths and MO and Pauling bond orders, gratuitous assumptions are necessary to rationalize the qualitative difference in behavior of 2-naphthyl acetate and 2-anthryl acetate in the Fries reaction. On the other hand, the chemical results obtained in the present investigation are consistent with the physical evidence and rationalizations herein presented.

Finally, it should be emphasized that our theoretical conclusions lead to the prediction that extrapolations from benzene to naphthalene to "higher" condensed aromatic hydrocarbons will be most successful if limited to angular benzologs, *i.e.*, phenanthrene...hexahelicene, etc. The linear acenes (anthracene, naphthacene, pentacene, hexacene, etc.) appear to comprise a separate series with widely different properties from their angular isomers. Although we do not claim that this is an

(23) The only exception, to our knowledge, is represented by the bond lengths of anthracene, as determined by X-ray methods. However, bond lengths are not linear functions of bond orders; instead, a smooth-curve relationship has been said to exist. We regard this relationship as less than firmly established for two reasons: (a) the accuracy of all but a very few of the measured "aromatic" bond lengths in the bond-order region of 1.50 to 1.75 does not fulfill present standards of reliability, as outlined by Cruickshank, *Acta Cryst.*, **13**, 774 (1960), and (b) virtually no accurate bond length data exist for the bond-order regions of 1.0-1.5 and 2.0-3.0.

(24) E. Clar, *Ber.*, **72B**, 1817 (1938).

(25) M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, **78**, 4765 (1956).

original discovery, we do believe that the above differences have not received sufficient emphasis and recognition.

Experimental²⁶

2-Anthrol, prepared²⁷ by alkali fusion of sodium 2-anthracenesulfonate, was acetylated²⁸ to give *2-anthryl acetate*. *Methyl 1- and 2-anthryl ketones* (IIIb and IVb)⁸ were prepared from methyl 9-anthryl ketone.²⁹

2-Methoxyanthracene. This compound was prepared by treatment of 2-anthryl acetate with dimethyl sulfate,¹⁰ but the preferred method was *via* ring closure of 2-(4'-methoxybenzyl)benzoic acid^{30,31} to the methoxyanthrone followed by zinc-alkali reduction.³²

A. From 2-Anthryl Acetate. A slurry of 12 g. (0.051 mole) of 2-anthryl acetate and 16.5 g. (0.131 mole) of dimethyl sulfate in 300 ml. of acetone was added dropwise, with stirring, to 20 g. of sodium hydroxide dissolved in a minimum amount of water. Water (15 ml.) was added, and the mixture was heated (steam bath) for 2 hr. The precipitate which formed when the mixture was poured into water was recrystallized three times from benzene to yield 7.35 g. (69%) of large, shiny, cream-colored flakes, m.p. 183-186°. Sublimation raised the melting point to 184.8-185.3°, lit. m.p. 175-178°.³³

B. From 2-(4'-Methoxybenzoyl)benzoic Acid. A mixture of 10 g. of 2-(4'-methoxybenzoyl)benzoic acid,³¹ 100 g. of zinc dust, 500 ml. of water, and 150 ml. of 25% sodium hydroxide was heated (stirring) on a steam bath for 3 days.³⁴ The residue left on hot filtration was extracted twice with hot water. Acidification with hydrochloric acid produced a light pink precipitate, which was washed with water, dried, and recrystallized once from benzene and once from aqueous acetic acid (methanol also is suitable) to give 7.1 g. (75%) of 2-(4'-methoxybenzyl)benzoic acid as white needles, m.p. 117.5-119°.

If the reduction is terminated after 7 hr., (4-methoxyphenyl)phthalide (72%, m.p. 117-118°) is obtained; this compound, which is deceptively similar to the above benzylbenzoic acid (m.m.p. 97-109°), is recovered unchanged on attempted ring closure with sulfuric acid. If recycled in the prolonged reduction, the phthalide is converted to 2-(4'-methoxybenzyl)benzoic

(26) Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected.

(27) P. Ferrero and A. Conzetti, *Helv. Chim. Acta*, **11**, 1152 (1928).

(28) J. Hall and A. G. Perkin, *J. Chem. Soc.*, **123**, 2029 (1923).

(29) C. Merritt and C. E. Braun, *Org. Syn.*, **30**, 1 (1950).

(30) F. F. Blicke and O. J. Weinkauff, *J. Am. Chem. Soc.*, **54**, 1460 (1932).

(31) C. Nourrisson, *Ber.*, **19**, 2103 (1886).

(32) E. L. Martin, *J. Am. Chem. Soc.*, **58**, 1438 (1936).

(33) C. Liebermann and A. Hagen, *Ber.*, **15**, 1427 (1882).

(34) L. F. Fieser and M. Fieser, *J. Am. Chem. Soc.*, **57**, 1679 (1935).

acid. Nourrisson,³¹ who obtained the phthalide (m.p. 116–117°) by zinc–hydrochloric acid reduction of 2-(4'-methoxybenzoyl)benzoic acid, also reported that zinc–ammonia reduction of the benzoylbenzoic acid produced the benzylbenzoic acid, m.p. 110–111°. Blicke³⁰ obtained this same benzylbenzoic acid by methylation of 2-(4'-hydroxybenzyl)benzoic acid.

2-Methoxy-9-anthrone (m.p. 93.4–96°, lit. m.p. 94–95°) was prepared³⁰ from 2-(4'-methoxybenzyl)benzoic acid in 55% yield.

A mixture of 25 g. of 2-methoxy-9-anthrone, 100 g. of "activated" zinc dust, 1.4 l. of 2 *N* sodium hydroxide, and 600 ml. of benzene (or toluene)³² was refluxed (steam bath) with stirring for 20 hr. The water layer first became red, but changed to tan when the reaction was complete. The supernatant liquid was decanted, the zinc residue was extracted with three 50-ml. portions of boiling benzene, and all the liquid portions were combined and filtered hot. The benzene layer was removed with a siphon, distilled to 400 ml., filtered hot, cooled, and worked up to yield 19.6 g. (84%) of 2-methoxyanthracene as shiny, light cream-colored flakes, m.p. 183–186°.

Methyl 2-Hydroxy-1-anthryl Ketone (Vb). *A. Nitrobenzene Solvent.* A mixture of 7.0 g. (0.030 mole) of 2-anthryl acetate and 8.5 g. (0.036 mole) of anhydrous aluminum chloride was cooled (ice bath) for 5–10 min. On addition of 25 ml. of dry nitrobenzene the mixture very quickly turned dark. The flask was swirled for 5 min. in the ice bath and allowed to stand for 25 min. at room temperature. Crushed ice (about 250 g.) was added, the flask was swirled occasionally for 15 min. and allowed to stand until the ice had melted. Nitrobenzene was removed from the brown mixture by steam distillation with a Wallenberger³⁵ apparatus. Filtration of the cooled residue gave a dark solid which was extracted with 5% sodium hydroxide. The alkaline extract was filtered and acidified with hydrochloric acid. Acidification of a second alkaline extract produced a solid which was extracted continuously with hexane until the extract was no longer yellow. The hexane solution was evaporated under reduced pressure and the residue was carefully crystallized from aqueous ethanol.³⁶ Slow cooling afforded 3.4 g. of yellow needles, m.p. 116–117°; the mother liquor yielded a second fraction which was recrystallized to give 0.65 g., m.p. 115.5–117°; total yield 58%. An analytical sample, m.p. 115–116.5°, was prepared by three recrystallizations from aqueous ethanol and by two from ethanol.

Anal. Calcd. for C₁₆H₁₂O₂: C, 81.33; H, 5.11. Found: C, 81.57; H, 5.18.

B. At 120–130° without Solvent. An intimate mixture of 1.10 g. of anhydrous aluminum chloride and 2.12 g. of 2-anthryl acetate was heated for 0.5 hr. in an oil bath at 120–130°. After decomposition of the complex with ice and hydrochloric acid, the mixture was filtered, and the green-brown residue was extracted with 10% sodium hydroxide solution.³⁷ Filtration and acidification of the alkaline solution produced a yellow-

(35) F. T. Wallenberger, W. F. O'Connor, and E. J. Moriconi, *J. Chem. Educ.*, **36**, 251 (1959).

(36) A small amount of tar occasionally formed in the hot solution and was removed by filtration.

(37) In some instances the product was extracted first with boiling benzene to yield a small amount of crude VIb, m.p. 210–222° dec.

green solid which was extracted (Soxhlet) with ether. Addition of petroleum ether (b.p. 30–60°) to this dark brown extract caused the separation of a brown gum. The solution was decanted and the petroleum ether treatment was repeated twice again. Evaporation of the solvent and sublimation of the residue at reduced pressure yielded a yellow powder, m.p. 96–101°, which when crystallized from aqueous ethanol produced yellow needles which did not depress the melting point of the ketone prepared as in A. An equally small amount of VIb (about 30 mg.) could be obtained from the brown gum. In one instance, methylation of the crude product with dimethyl sulfate and sodium hydroxide produced (as the major product) 2-methoxyanthracene, apparently from hydrolysis of unreacted 2-anthryl acetate.

Methyl 3-Hydroxy-2-anthryl Ketone (VIb). A pulverized mixture of 1.5 g. (0.0064 mole) of 2-anthryl acetate and 1.8 g. (0.013 mole) of anhydrous aluminum chloride was heated for 1.5 hr. in an oil bath at 145°. The brownish black complex was decomposed with ice and hydrochloric acid. A boiling ethanol solution of the yellow-brown residue was treated with Norit, filtered, and water was added to the cloud point. The resulting yellow solid was recrystallized four times from benzene–petroleum ether (b.p. 30–60°) to give 0.04 g. (3%) of greenish yellow leaflets, m.p. 228–233° dec. Two more recrystallizations gave tan prisms, m.p. 228–232° dec., which were recrystallized twice from benzene–hexane to give yellow prisms,³⁸ m.p. 227.5–229° dec. An analytical sample (m.p. 226–227° dec., lit.¹¹ m.p. 218–219° dec.) was prepared by another recrystallization from benzene.

Anal. Calcd. for C₁₆H₁₂O₂: C, 81.33; H, 5.11. Found: C, 81.03; H, 5.01.

Methyl 2-Methoxy-1-anthryl Ketone (VIIb). A solution of 3.0 g. (0.013 mole) of Vb and 5.3 g. (0.042 mole) of dimethyl sulfate in 120 ml. of acetone was added dropwise with stirring to 6 g. of sodium hydroxide in a minimum amount of water. The mixture was diluted with 10 ml. of water, heated for 1 hr. on a steam bath, and poured into 700 ml. of water. The filtered precipitate was recrystallized from aqueous methanol to yield 2.9 g. (91%) of VIIb as large, flat, fawn-colored needles, m.p. 102–103.5°. The analytical sample, m.p. 102.5–104°, was prepared by three more recrystallizations from aqueous methanol and two from methanol.

Anal. Calcd. for C₁₇H₁₄O₂: C, 81.57; H, 5.63. Found: C, 81.86; H, 5.47.

Methyl 3-Methoxy-2-anthryl Ketone (VIIIb). This compound was prepared (70% yield) as above. Thus, 0.20 g. (0.85 mmole) of VIb and 0.30 g. (2.3 mmole) of dimethyl sulfate in 40 ml. of acetone was added dropwise with stirring to 0.30 g. of sodium hydroxide in a minimum of water. The mixture was diluted with 80 ml. of water and extracted with three 30-ml. portions of ether. Evaporation of the dry extracts followed by several recrystallizations of the residue from aqueous ethanol and from ethanol afforded the analytical sample as yellow flakes, m.p. 95–96°, which depressed the melting point of VIIb.

(38) Another crystal modification (red needles) sometimes formed which could be converted to the yellow prisms by recrystallization from benzene, and which did not depress the melting point of the yellow prisms.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.57; H, 5.63. Found: C, 81.88; H, 5.77.

Methyl 3-Acetoxy-2-anthryl Ketone. A mixture of 0.30 g. (1.3 mmoles) of VIb, 10 ml. of acetic anhydride, and 5 drops of pyridine was refluxed for 1 hr., poured onto ice, and stirred until the ice had melted and a solid had formed. Two recrystallizations from aqueous ethanol and one from aqueous acetic acid (followed by treatment with Norit in isopropyl alcohol) produced 0.25 g. (71%) of golden flakes, m.p. 163–165°. An analytical sample, m.p. 163.5–164.5°, was obtained by further recrystallizations from ethanol.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.72; H, 5.24.

Methyl 2-Acetoxy-1-anthryl Ketone. This compound was prepared, as above, by refluxing 0.10 g. (0.40 mmole) of Vb in 10 ml. of acetic anhydride and 2 drops of pyridine for 1 hr. After treatment with ice and recrystallization from aqueous ethanol, 0.10 g. (83%) of fine, straw-colored needles, m.p. 135–136°, was obtained. Further recrystallizations produced an analytical sample, m.p. 131.5–132.5°.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.87; H, 4.95.

Formylation of 2-Methoxyanthracene. A solution of 1.7 g. of N-methylformanilide and 2.1 g. of phosphorus oxychloride, which had been standing for 0.5 hr. at room temperature, was poured onto 1.0 g. (5.0 mmoles) of 2-methoxyanthracene. The dark red mixture became warm, and tiny bubbles were evolved. After the mild evolution of gas subsided, the flask was heated in an oil bath at 50–60° for 1.5 hr. The dark solution was poured into ice-water, and 1 ml. of concentrated hydrochloric acid was added. Trituration afforded a yellow-green solid, whose solution in 75 ml. of hot ethanol was decolorized (Norit), treated with water to the cloud point, and slowly cooled to yield 0.80 g. (70%) of a mixture of yellow needles (m.p. 170–180°)³⁹ and golden yellow, transparent flakes (m.p. 110–117°)³⁹ in approximately equal amounts. This mixture was extracted with several portions of cold ether, and the insoluble residue was recrystallized twice from a small volume of boiling ether, three times from ethanol, and twice from methanol to yield 2-methoxy-1-anthraldehyde (VIIa) as yellow crystals, m.p. 192–194.5°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.11. Found: C, 80.45; H, 4.81.

The above ether extracts were concentrated to a small volume, filtered, and evaporated. The residue was fractionally recrystallized six times from aqueous ethanol and once from ethanol to yield 3-methoxy-2-anthraldehyde (VIIIa) as transparent yellow flakes, m.p. 116–117°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.11. Found: C, 80.88; H, 5.20.

A still tedious, but perhaps more efficient, separation of VIIa and VIIIa was effected by Soxhlet extractions of the crude product with hexane followed by recrystallization of the insoluble residue from benzene. A fairly pure sample of VIIa thus was obtained as flat, hexagonal, orange crystals. Concentration of the hexane solution then afforded fairly pure VIIIa as long, flat, pale yellow crystals.

(39) Determined on a few crystals which were separated manually from the mixture.

Ineffective (or inferior) methods of separation included fractional recrystallizations from a variety of solvents and column chromatography with alumina or cellulose.

2-Hydroxy-1-anthraldehyde (Va). To a solution of 0.50 g. (2.1 mmoles) of VIIa in 10 ml. of glacial acetic acid at room temperature was added 2 ml. of 47% hydrobromic acid. The solution was refluxed (with occasional swirling) for about 40 min., and the original deep red color deepened to orange-black. Filtration of the cooled mixture afforded greenish crystals, and more green solid was obtained from the diluted filtrate. The combined solids were extracted twice with dilute potassium hydroxide, and the filtered alkaline extracts were acidified with hydrochloric acid to yield a yellow precipitate which was crystallized from aqueous ethanol to give 0.12 g. (47%) of fine yellow needles, m.p. 167–169°. Sublimation yielded an analytical sample, m.p. 166.5–167°, identical with the product from a Gattermann reaction on 2-anthrol.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.53. Found: C, 81.25; H, 4.62.

3-Hydroxy-2-anthraldehyde (VIa). A solution of 0.30 g. (1.2 mmoles) of VIIIa in 5 ml. of glacial acetic acid was treated with 2 ml. of 47% hydrobromic acid. The red mixture was heated to reflux, allowed to cool, and poured on ice. The brownish yellow precipitate was washed and dissolved in 5% sodium hydroxide. The blood red alkaline solution was filtered, acidified with hydrochloric acid, and digested for 1 hr. on a steam bath. The crude product was crystallized from ethylene dichloride to yield 0.11 g. (38%) of VIa as reddish orange spears, m.p. 222–232° dec. Five more recrystallizations produced an analytical sample, m.p. 228–231° dec.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.06; H, 4.53. Found: C, 81.50; H, 4.78.

Chromic Anhydride Oxidations. A. 3-Methoxy-2-anthraldehyde (VIIIa). To 0.16 g. (0.68 mmole) of VIIIa in 5 ml. of refluxing glacial acetic acid 0.3 g. of chromic anhydride in 3 ml. of 50% acetic acid was added dropwise. The exothermic reaction produced a dark green solution. After about 3 min., addition of hot water precipitated 0.087 g. (53%) of a light yellow solid, m.p. 197–198°. One recrystallization from ethanol gave light yellow needles of 2-methoxyanthraquinone, m.p. 200.5–202°, identical with an authentic sample.

B. 2-Methoxy-1-anthraldehyde (VIIa). This compound (0.10 g., 0.42 mmole), oxidized as above, yielded a cream-colored crude product which turned brownish violet on drying in air. Two recrystallizations from benzene afforded impure 2-methoxyanthraquinone-1-carboxylic acid as small, yellow-tan needles,⁴⁰ m.p. 259–268.5° dec., soluble in sodium carbonate solution.

Permanganate Oxidations.¹⁰ A. 2-Methoxy-1-anthraldehyde (VIIa). In an ice bath, 1.0 g. (4.2 mmoles) of VIIa in 160 ml. of pyridine was stirred with 0.6 g. of potassium hydroxide in 60 ml. of water. The ice bath was removed, and a solution of 3.2 g. of potassium permanganate in 80 ml. of water was added dropwise over 1 hr. at 15–25°. The mixture was stirred for 0.5 hr. at room temperature, excess permanganate was

(40) This sample was probably contaminated with some of the corresponding hydroxy compound, m.p. 265°. ¹³

decomposed with a minimum of solid sodium sulfite, and the mixture was filtered. From the manganese dioxide 0.1 g. of unreacted VIIa was obtained. Acidification of the filtrate yielded a fine yellow precipitate, more of which was obtained by extracting the filtrate three times with ether. The combined solids were treated with 10% sodium bicarbonate. Acidification of the filtered mixture produced a precipitate which was crystallized from benzene to yield 0.25 g. of a mixture of yellow flakes and pale yellow needles. Only the needles exhibited a red vat test. Fractional crystallization from benzene produced the more soluble yellow flakes, m.p. 204–204.5°. Several recrystallizations gave an analytical sample of XI, m.p. 204–205° dec.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.79. Found: C, 75.73; H, 4.78.

The yellow needles were purified similarly to give 2-methoxyanthraquinone-1-carboxylic acid, m.p. 282–285° dec., identical with an authentic sample prepared by Marschalk's¹³ procedure, lit. m.p. 275–276° dec.

B. 3-Methoxy-2-anthraldehyde (VIIIa). A procedure similar to that above was applied to 0.50 g. (2.1 mmoles) of VIIIa in 80 ml. of pyridine with 0.3 g. of potassium hydroxide in 30 ml. of water; potassium permanganate (1.64 g.) in 140 ml. of water was added during 1 hr. The product was crystallized from benzene-hexane to yield 0.11 g. (m.p. 163–177°) and, from the mother liquor, 0.14 g. (m.p. 163–165° dec.) of yellow crystals. Further recrystallizations and a final sublimation produced the presumed XII, m.p. 162–163°, which gave no vat test; the amount of this sample was too small to permit a combustion analysis.

Haloform Reaction of Methyl 2-Methoxy-1-anthryl Ketone (VIIb). To 0.40 g. (1.6 mmoles) of VIIb at room temperature was added 49 ml. of potassium hypochlorite solution⁴¹ prepared from 10 g. of calcium hypochlorite (HTH). The mixture was stirred vigorously (some heat evolved) and then heated at 70–75° for 1.5 hr. Excess hypochlorite was decomposed with acetone, the mixture was filtered, and the filtrate was acidified to give 50 mg. of an acid, m.p. 265–269° dec. Two sublimations produced yellow needles of 2-methoxyanthraquinone-1-carboxylic acid, m.p. 282–286° dec., identical with an authentic sample.¹³ The residue from the above filtration was crystallized from absolute ethanol to give 0.18 g. of greenish yellow flakes, m.p. 173–177°, which did not give a vat test, and which contained halogen. Five more recrystallizations afforded the presumed X, m.p. 177–179°.

Anal. Calcd. for $C_{17}H_{11}O_2Cl_3$: Cl, 30.13. Found: Cl, 29.02.

In another reaction 2.0 g. (8.0 mmoles) of VIIb in 160 ml. of methanol was treated with 130 ml. of potassium hypochlorite solution prepared from 2 g. of calcium hypochlorite.⁴¹ The temperature did not exceed 50°, and at the end of 1.5 hr. the mixture was cooled to room temperature and stirred for another 4 hr. A saturated solution of sodium bisulfite was used to decompose excess hypochlorite. Filtration afforded the insoluble trichloromethyl ketone which, when extracted with boiling methanol, produced 0.2 g. of a soluble mixture of by-products (white, red, and yellow crystals, m.p. 163–187°) which was not further investigated.

(41) M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

Recrystallizations of the residue from ethanol gave 0.59 g. of X, m.p. 175–181°.

Hydrolysis of Trichloromethyl 2-Methoxy-1-anthryl Ketone (X). The trichloro compound, 0.49 g. (1.4 mmoles), in aqueous ethanolic potassium hydroxide was heated for 3 hr. on a steam bath. 2-Methoxyanthracene (identical with an authentic sample) separated from the alkaline solution. Acidification of the filtrate yielded, after purification, a lesser amount of XI, m.p. 204–205° dec., which was identical with the product obtained by permanganate oxidation of VIIa. A better yield (66 mg. from 0.10 g. of X) of XI was obtained when the reaction mixture was heated for only 1 hr.

*1-Anthraldehyde (IIIa).*¹⁰ To a stirred mixture of 5.3 g. (0.024 mole) of methyl 1-anthryl ketone^{8,29} and 3 g. of potassium hydroxide in 120 ml. of water and 300 ml. of pyridine at 10–15° was added, over a period of 2 hr., 12 g. of potassium permanganate in 400 ml. of water. Excess permanganate was decomposed with solid sodium sulfite, and the mixture was filtered, acidified, and allowed to stand overnight. The mixture of red and yellow crystals, m.p. 125–170°, was recrystallized several times from ethanol (Norit) to give 0.1 g. of 1-anthroic acid, m.p. 248–252°. Continuous ether extraction of the above filtrate removed a red oil, which was treated with 10% sodium bicarbonate solution. The alkaline mixture was shaken with ether. The greenish yellow flakes which collected at the interface of the layers were dissolved in water. The solid obtained on acidification with hydrochloric acid was recrystallized several times to produce 1.05 g. of yellow-red needles, which melted at 139°, then resolidified, and melted again at 153–155°. Several recrystallizations from benzene-cyclohexane and from benzene produced orange needles of 1-anthrylglyoxylic acid, m.p. 131°, partial resolidification at 135°, m.p. 142–144° dec.

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 77.01; H, 4.15.

1-Anthrylglyoxylic acid (0.50 g., 2.0 mmoles) and 0.5 ml. of N,N-dimethyl-*p*-toluidine were heated at 80° for 10 min. as tiny bubbles evolved. Over 0.5 hr. the temperature was raised to 90–100° and the solution was kept at that temperature until decarboxylation ceased; the deep red solution then was extracted with a mixture of 20 ml. of ether and 10 ml. of hydrochloric acid. The thoroughly washed ether layer was evaporated and the residue was crystallized from aqueous ethanol to give 0.34 g. (83%) of flat, yellow rods, m.p. 129–134°. Recrystallizations from aqueous ethanol and from cyclohexane, followed by sublimation, gave flat, transparent yellow crystals of IIIa, m.p. 134–135°, lit. m.p. 125.6–127.5°⁷ and 125–128°.⁹

Anal. Calcd. for $C_{15}H_{10}O$: C, 87.35; H, 4.89. Found: C, 87.18; H, 4.92.

2-Anthraldehyde (IVa). *A. From Methyl 2-Anthryl Ketone (IVb).* As above, 5.6 g. (0.025 mole) of IVb,^{8,29} 800 ml. of pyridine, and 3 g. of potassium hydroxide in 100 ml. of water were treated with 12.5 g. of potassium permanganate in 400 ml. of water at 10–15°. After 2.5 hr. the mixture was processed as above, acidification of the filtrate yielding 1.4 g. of IVb and 0.7 g. of 2-anthroic acid, m.p. 273–276° dec. Continuous extraction of the filtrate with ether, extraction of the ether with bicar-

bonate solution, and filtration and acidification of the bicarbonate extract gave a yellow precipitate. Recrystallization from ethanol and from methyl ethyl ketone-hexane afforded 1.0 g. of yellow and red crystals of the presumed 2-anthrylglyoxylic acid, m.p. 240–284° dec., which was not purified further.

A solution of 0.5 g. of the glyoxylic acid in 0.5 ml. of N,N-dimethyl-*p*-toluidine was heated gently until decarboxylation commenced. The temperature was raised from 150 to 190° over 0.5 hr. until gas evolution ceased. Work-up as above yielded a product which was crystallized from ethanol to give 0.3 g. of yellow flakes, m.p. 208.5–211.5°. Several recrystallizations from absolute ethanol gave impure IVa as pale yellow flakes, m.p. 209–210.5°, lit.⁷ m.p. 203–204°. Combustion analysis indicated that this sample was contaminated with anthracene.

B. McFadyen-Stevens Method. Methyl 2-anthroate, m.p. 193.5–194° (lit. m.p. 128°⁴² and 192–193°⁴³), was prepared by esterification of the acid in dry methanol with hydrogen chloride. This ester (26 g., 0.11 mole) and 150 ml. of hydrazine hydrate (85%) were refluxed for 36 hr. To the cooled mixture 600 ml. of water was added. Filtration afforded 20 g. (77%) of yellow crystals, m.p. 245–248.5° dec. Four recrystallizations from pyridine produced an analytical sample of 2-anthroylhydrazine as long, flat, yellow plates, m.p. 241–244° dec., with subsequent resolidification.

Anal. Calcd. for C₁₅H₁₂N₂O: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.10; H, 5.04; N, 12.05.

To 20 g. (0.085 mole) of 2-anthroylhydrazine in 100

(42) K. Lauer, *Ber.*, 70B, 1288 (1937).

(43) F. H. C. Stewart, *Australian J. Chem.*, 13, 478 (1960).

ml. of pyridine at room temperature was added dropwise with stirring 15 g. (0.085 mole) of benzenesulfonyl chloride. After 15 min. a clear solution resulted, but stirring was continued for 3 hr. The solution was poured onto ice to give 28.8 g. (90%) of yellow solid, m.p. 250–255° dec. Five recrystallizations from acetic acid and one from pyridine-cyclohexane gave 2-anthroylbenzenesulfonylhydrazide as small, light yellow flakes, m.p. 237.5–239° dec.; mixture melting point with 2-anthroylhydrazine was 209–220° dec.

Anal. Calcd. for C₂₁H₁₆N₂O₃S: C, 67.01; H, 4.29; N, 7.44; S, 8.50. Found: C, 66.81; H, 4.32; N, 7.50; S, 8.35.

To a stirred mixture of 11.3 g. (0.0301 mole) of 2-anthroylbenzenesulfonylhydrazide and 200 ml. of ethylene glycol heated to 165°, 8 g. of sodium carbonate was added in one portion. After 1 or 2 min. the vigorous reaction had subsided. Water was added to the cooled mixture, and the gelatinous mass was filtered. The product was washed, dried, and extracted continuously with ether. The residue obtained on evaporation was recrystallized from benzene-ethanol to yield impure IVa, m.p. 199–206°. Sublimation gave 2.9 g. (45.3%) of yellow crystals, m.p. 199–203°. Five recrystallizations from ethyl acetate-ethanol produced an analytical sample of IVa, m.p. 201.5–202.9°, lit. m.p. 203–204°.⁷

Anal. Calcd. for C₁₅H₁₀O: C, 87.35; H, 4.89. Found: C, 87.15; H, 4.83.

Acknowledgment. We wish to thank the National Science Foundation and the University of Massachusetts Research Council for grants in support of this work.

New Aspects of the Hofmann-Loeffler N-Chloramine Rearrangement in Acetic Acid

Robert S. Neale and Maria R. Walsh

Contribution from Union Carbide Research Institute, Tarrytown, New York.
Received August 20, 1964

The photolytic rearrangement I → IV of N-chlorodi-n-butylamine (I) in acetic acid was carried out under several sets of reaction conditions in order to determine why the process requires an excess of sulfuric acid to occur in good yield. The optimum conditions for the synthetic utilization of the chloramine rearrangement in acetic acid were thereby defined. The enhancement in yield of the Hofmann-Loeffler end product V with increasing acidity³ was confirmed, but the over-all reaction rate was found to decrease with increasing acidity in contrast to an earlier report.³ Excess sulfuric acid reduces the rate of a nonradical disproportionation of I to N,N-dichloro-n-butylamine; in the absence of externally added impurities, the dichloramine is believed to be the primary initiator of the rearrangement I → IV. The yield of V falls rapidly under those conditions which facilitate the accumulation of small amounts of the dichloramine in the reaction mixture during photolysis.

There have been many reports in the recent literature of synthetic applications of the Hofmann-Loeffler N-chloramine rearrangement,¹ and through the efforts of two groups of investigators^{2,3} the mechanism of this free-radical chain process has been adequately defined with respect to the propagation sequence (II → IV);

this involves nitrogen cation radicals R₂NH⁺ (aminium radicals, II) as key intermediates. In order to define more precisely than previously³ the requirement of an excess of sulfuric acid in the Hofmann-Loeffler rearrangement, and in other reactions involving aminium radicals generated from N-chloramines,⁴ we have

(1) M. E. Wolff, *Chem. Rev.*, 63, 55 (1963).

(2) S. Wawzonek and P. J. Thelen, *J. Am. Chem. Soc.*, 72, 2118 (1950); S. Wawzonek and T. P. Culbertson, *ibid.*, 81, 3367 (1959).

(3) E. J. Corey and W. R. Hertler, *ibid.*, 82, 1657 (1960).

(4) (a) R. S. Neale and R. L. Hinman, *ibid.*, 85, 2666 (1963); (b) R. S. Neale, *ibid.*, 86, 5340 (1964).