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STRUCTURE OF THE MONOÖZONIDE OF 9,10-DIMETHYLANTHRACENE

A TRANSANNULAR OZONE ADDUCT

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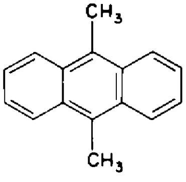
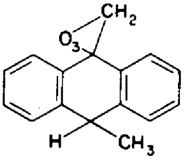
Abstract—9,10-Dimethylanthracene and 9-methoxy-10-methylanthracene each absorb one mole of ozone to produce monoözonides in high yield. These were shown to be 9,10-transannular ozone adducts by NMR spectroscopy. A comparison with other anthracene derivatives in their behavior toward ozone is made.

INTRODUCTION AND DISCUSSION

It was reported recently by de Bruyn[3] that 9,10-dimethylanthracene (I) reacts with ozone to form a stable monoözonide, for which de Bruyn proposed structure II rather than III. Since the only primary ozonide reported in the literature comes from the symmetrical and somewhat sterically hindered *trans*-1,2-di-t-butylethylene[4] and is stable only below -60°, and since the unsymmetrical 1,1-diphenylethylene apparently does not give a stable primary ozonide (which would be sterically similar to II), but is cleaved immediately to yield an ordinary ozonide,[5] it seemed more likely to us that some form of III (either V or VI) was correct for the stable monoözonide of I. We also felt that structure IV, a possible rearrangement product of III, should be considered.

Repetition of de Bruyn's[3] work showed his results to be accurate. However, the following observations should be reported. 9,10-Dimethylanthracene (I) reacts


I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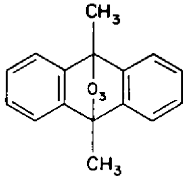
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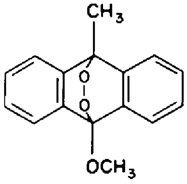
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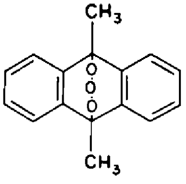
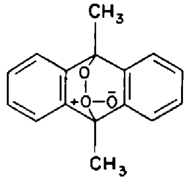

V


VI

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[1] A portion of the organic chemistry laboratory research was done at Karlsruhe in 1960.

[2] To whom requests for reprints should be addressed.

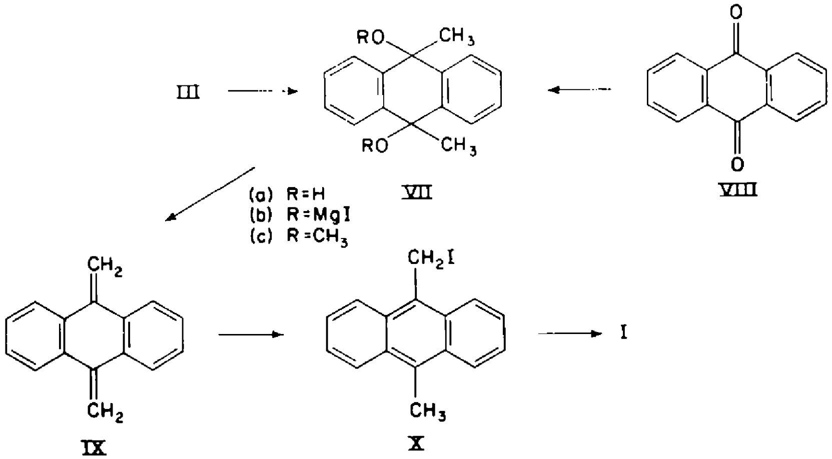
[3] P. de Bruyn, *Bull. Soc. Chim. Belg.* **69**, 328 (1960).

[4] R. Criegee and G. Schröder, *Chem. Ber.* **93**, 689 (1960). For definition of "Primary" (or "initial") ozonide, see R. Criegee, *Rec. Chem. Progr.* **18**, 111 (1957).

[5] R. Criegee, *Adv. in Chem. Ser.* **21**, 135 (1959).

quantitatively with one mole of ozone at —78° in a number of solvents (methylene chloride in addition to those reported by de Bruyn) to afford high yields of a crystalline ozonide. Using an ozone–nitrogen mixture rather than ozone–oxygen, it was shown, within experimental error, that no oxygen was evolved in the major reaction. Contrary to the report of de Bruyn,[3] a trace of pyridine is not necessary for the formation of the ozonide, although it probably helps to stabilize the ozonide against decomposition. de Bruyn[3] reported that cuprous chloride and cobaltous chloride reduced the ozonide in methanol solution to 9,10-dimethoxy-9,10-dimethyl-9,10-dihydroanthracene (VIIc) and stated that this product could be expected from II because of other rearrangements known to occur with these reagents. We have shown that the same product can be obtained from either catalytic hydrogenation (Pd on $CaCO_3$) in methanol or from reduction with potassium iodide in methanol. These reagents would not be expected to cause rearrangements and, therefore, give evidence for structure III over II.

Actually all of the chemistry reported by de Bruyn[3] for the monoözonide is more easily explained by structure III than by II. His best evidence for II was iodide (KI in acetic acid) reduction of the ozonide to 9-iodomethyl-10-methylanthracene (X) followed by stannous chloride reduction back to I. We have shown that X is the same compound previously obtained by addition of methylmagnesium iodide to anthraquinone (VIII) followed by hydriodic acid reduction.[6] From III and VIII, the intermediates must be VIIa and VIIb, respectively, which go on to X, probably through intermediate IX.



Convincing proof for the assignment of structure V to the monoözonide of I was obtained by NMR spectroscopy, which showed only one type of hydrogen besides the aromatic ring hydrogens. Solutions of V rapidly decomposed at room temperature to a substance, shown by NMR spectroscopy to be compound IV. This is discussed in detail under NMR Results.

In order to see if other suitably 9,10-substituted anthracenes form transannular ozonides, 9-methoxy-10-methylanthracene (XI) was ozonized. It reacted quantitatively with one mole of ozone at —78° with release of essentially no oxygen (using an ozone-nitrogen mixture) to give a colourless, crystalline ozonide which decomposed

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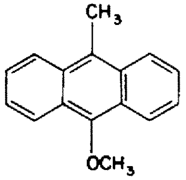
[6] D. D. Phillips and J. Cason, *J. Amer. Chem. Soc.* 74, 2934 (1952).

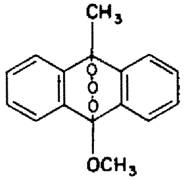
above —20°. The ozonide was shown to be transannular (XII) by NMR spectroscopy. Solutions of XII decomposed at room temperature to give XIII. This is discussed in detail under NMR Results.

It is interesting to compare the action of ozone on 9,10-dimethylanthracene (I) and 9-methoxy-10-methylanthracene (XI) on the one hand with anthracene and the 9,10-dihaloanthracenes on the other hand.

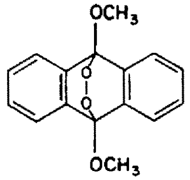
In the presence of nucleophilic solvents like methanol, anthracene and the dihaloanthracenes are attacked at the center ring by ozone with loss of oxygen to give high yields of anthraquinone, whereas in the absence of these solvents the major attack occurs at the outer ring(s).[7,8] There is no such solvent effect with 9,10-dimethylanthracene (I) and 9-methoxy-10-methylanthracene (XI), where the ozone attack appears to occur exclusively at the center ring. It is logical to assume that in all cases the center ring reaction involves first the reversible electrophilic attack of ozone to give intermediate XIV which is stabilized by nucleophilic solvents. Where R is halogen or hydrogen, these groups leave as anions, along with oxygen, to give XV, or some solvent stabilized form thereof, which may be attacked by ozone or the nucleophilic solvent to eventually give anthraquinone. Where R is hydrogen, ozone aids in the removal of hydride ion, producing hydroxyl ion and oxygen.[8] Where R is methyl, however, the leaving power is very low and thus XIV must stabilize itself by formation of the transannular ozonide V.



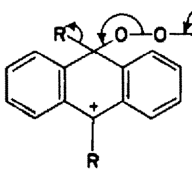
XI



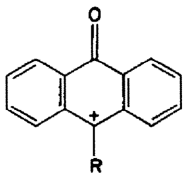
XII



XIII



XIV



XV

The lack of a solvent effect with 9,10-dimethylanthracene is probably due to the methyl groups activating the central ring to such an extent that ozone attack occurs exclusively there; the equilibrium is in favor of XIV in this case, rather than away from it. The greatest solvent effect occurs with 9,10-dibromoanthracene, where the centre ring is somewhat deactivated and XIV must be solvent stabilized in order for the equilibrium to lie in its direction. Otherwise ozone leaves and attacks predominantly an outer ring.[7] In this connection it is interesting to note that 9-nitroanthracene also shows little or no solvent effect, the major attack occurring at the outer rings in all cases. Here the nitro group greatly deactivates both the centre ring and

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[7] F. Dobinson and P. S. Bailey, *Tetrahedron Letters* No. 13, p. 14 (1960).

[8] F. Dobinson and P. S. Bailey, *Chem. & Ind.* 632 (1961).

intermediate XIV and the major reaction is outer ring attack, regardless of the solvent.

Other anthracenes, namely 9,10-diphenylanthracene, 9-phenylanthracene and 9,10-dinitroanthracene, have been ozonized, but have not been thoroughly studied, since complex mixtures of final products apparently are obtained in these cases. However, several mole-equivalents of ozone are absorbed in each case, and, in the one case tried, diphenylanthracene, oxygen was evolved during ozonation with an ozone–nitrogen mixture. Thus, no transannular ozonides apparently are produced, at least in appreciable amounts.

NMR RESULTS AND DISCUSSION

A proton magnetic resonance spectrum taken immediately on a freshly prepared solution of the ozonide of 9,10-dimethylanthracene (I) in methylene chloride at 28° showed in addition to the solvent peak at $\tau = 4{\cdot}66$, a large single peak at $\tau = 7{\cdot}97$, two small peaks at $\tau = 6{\cdot}32$ and 8·33 and a group of peaks centred about $\tau = 2{\cdot}48$. There were also two small peaks at 90 cps above and below the methylene chloride resonance which were attributed to splitting of the methylene peak by the natural abundance of C^{13}.

The solution had taken on a slight coloration immediately, indicating the occurrence of a reaction at 28°. This was further verified when the entire spectrum was swept repeatedly and it was observed that within a few minutes the peak at $\tau = 7{\cdot}97$ diminished until it became quite small while the peaks at $\tau = 6{\cdot}32$ and 8·33 grew rapidly and more fine structures became apparent in the resonance at $\tau = 2{\cdot}48$. When equilibrium had been established the peaks at $\tau = 6{\cdot}32$ and 8·33 were of nearly equal intensity and of approximately half the size of the original peak at $\tau = 7{\cdot}97$. These observations are consistent with the proposed structure V for the crystalline ozonide of I and for its decomposition in solution to compound IV. The original peak at $\tau = 7{\cdot}97$ is assigned to the methyl protons and the peaks at $\tau = 2{\cdot}48$ to the aromatic protons. The rapid change at 28° signifies decomposition. The peak at $\tau = 8.33$ is easily assigned to the methyl protons in IV and the peak at $\tau = 6{\cdot}32$ is attributed to the methoxy group. The decrease in symmetry from V to IV has a corresponding effect in increasing the complexity of the aromatic splittings at the lower field peaks. These assignments are compatible with typical methyl and methoxy chemical shifts in the proximity of aromatic rings and, in addition, the shift of the methyl resonance from $\tau = 7{\cdot}97$ to 8·33 in the decomposition of V to IV is reasonable in view of the steric rearrangement of oxygen atoms in the close proximity of the methyl group. The NMR spectrum of the ozonide in acetone also was obtained, but only after decomposition had occurred. Again however, peaks of equal intensity at $\tau = 8{\cdot}33$ and 6.32 and the group of peaks in the aromatic region of identical fine structure as found for the decomposition product in methylene chloride suggest structure IV as the decomposition product and hence V as the structure of the original ozonide.

In order to establish the structure of the ozonide more conclusively, a spectrum of the cold methylene chloride ozonolysis reaction mixture was obtained at −80° using a variable temperature apparatus, similar to one previously described,[9] to maintain the sample at the desired temperature. The NMR spectrum was quite simple and confirmed the first spectrum previously obtained at room temperature. Other than the solvent peak and its C^{13} satellites, the only peaks observed were the peak at $\tau = 7{\cdot}97$

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[9] J. C. Davis, Jr. and K. S. Pitzer, *J. Phys. Chem.* **64**, 886 (1960).

and a pair of overlapping peaks with no resolved fine structure at $\tau = 2{\cdot}66$ and $2{\cdot}48$. There was no evidence of additional peaks and splittings which would be observed for structure II, which has three different kinds of non-equivalent non-aromatic hydrogens. Likewise structure VI is ruled out in favor of V by this spectrum, since in this case the non-equivalence of the two transannular oxygen atoms would produce significantly different electronic environments at the two methyl groups. Thus, structure VI would be expected to show two different methyl peaks with a significant difference in chemical shift between them. Since the oxygen bridge of VI consists only of two atoms, one methyl peak might be expected in the vicinity of the methyl peak in the spectrum of IV.

The $-80°$ solution was allowed to warm to 28° whereupon the peak at $\tau = 7{\cdot}97$ began to disappear and was replaced by the peaks at $\tau = 6{\cdot}32$ and $8{\cdot}33$, as had previously been observed. After a period of four days the original peak at $\tau = 7{\cdot}97$ had not completely disappeared and a small peak at $\tau = 6{\cdot}86$ was present, probably resulting from further decomposition products which have not been identified.

The NMR spectrum of 9,10-dimethylanthracene (I) was also obtained and showed the expected aromatic fine structure centred around $\tau = 2{\cdot}05$ and a single methyl resonance at $\tau = 6{\cdot}88$. The lower shielding of the methyl protons in this compound as opposed to the higher shifts in the ozonide and its decomposition product is expected on the basis of the effects of the ring currents in the anthracene ring system.

The NMR spectrum of 9-methoxy-10-methylanthracene (XI) again showed the characteristic aromatic splitting about $\tau = 2{\cdot}05$ with the methoxy and methyl peaks appearing at $\tau = 5{\cdot}83$ and $6{\cdot}92$, respectively. The latter is coincident with the methyl resonance in 9,10-dimethylanthracene. The spectrum of the ozonized solution of 9-methoxy-10-methylanthracene (XI) at $-80°$ showed two overlapping aromatic peaks at $\tau = 2{\cdot}47$ and $2{\cdot}66$ similar to those of the ozonide of 9,10-dimethylanthracene. Peaks at $\tau = 6{\cdot}17$ and $7{\cdot}95$ were attributed to methoxy and methyl protons, the latter agreeing with the methyl shift in the ozonide of 9,10-dimethylanthracene (I). Again the slightest higher shift of the methoxy group as contrasted with the shift in the parent compound is consistent with the loss of ring current in the central ring of the ozonide, indicating that XII is the structure of this ozonide.

Upon warming the solution to 28° it was again observed that the peaks at $\tau = 6{\cdot}17$ and $7{\cdot}95$ disappeared and were replaced by a peak at $\tau = 6{\cdot}30$. The similarity of the ozonides and the coincidence of peaks at this position in the spectra of both decomposition products indicate that the decomposition product of XII is XIII. After a period of four days the NMR spectrum was much more complex with a number of peaks appearing in the region $\tau = 6{\cdot}30$ to $8{\cdot}33$. Apparently the subsequent decomposition products in this case are more varied; they have not been identified.

EXPERIMENTAL

NMR Spectra. The proton magnetic reasonance spectra were obtained at 60 Mcps on a Varian Associates DP-60 NMR Spectrometer System using $(CH_3)_4$ Si as an internal reference for the measurement of chemical shifts. In most cases the compound investigated was dissolved in the solvent and the spectra taken on the freshly prepared solution. In two cases the cold (—78°) ozonolysis reaction mixtures were used.

Preparation of ozonide of 9,10-dimethylanthracene (I)

De Bruyn's[8] preparations in various solvents were repeated with comparable results. In all cases one mole equivalent of ozone was readily absorbed, after which the rate dropped drastically. In another experiment a suspension of 0·6 g of I in 50 ml methanol and 15 ml methylene chloride (no pyridine present) was ozonized; 0·16 g (21 % yield) of the colorless crystalline ozonide precipitated.

Another time an ozone–nitrogen mixture was used and oxygen in the exit gases was determined as previously described.[10] Within experimental error, the results showed ozone attack to occur without oxygen release; the solvent was methylene chloride. The ozonide did not precipitate from methylene chloride, and in a similar run, using ozone–oxygen, a portion of the cold (−78°) solution was transferred by means of a precooled pipette to a precooled NMR tube and was kept at −78° until placed in the low temperature NMR probe. As stated elsewhere the NMR spectrum showed only the ozonide (V) to be present.

Reduction of the ozonide of I *to 9,10-dimethoxy-9,10-dimethyl-9,10-dihydroanthracene* (VIIc)

(a) A solution of 0·29 g ozonide (V) in 50 ml methanol was hydrogenated over palladium on calcium carbonate. After partial evaporation of the reaction mixture and addition of water, 0·087 g VIIc (m.p. 193–195°)[5] was obtained.

(b) To 10 ml methanol containing 0·2 g potassium iodide was added 0·075 g ozonide (V). After several hours the iodine formed was reduced with thiosulfate, the solution was extracted with methylene chloride and the extract was dried and evaporated. Recrystallization of the residue from methanol gave 0·05 g VIIc m.p. 194–195°.[5]

Reduction of the ozonide of I *to 9,10-dimethylanthracene* (I)

De Bruyn's[3] two step reduction of the ozonide to I was repeated. It was shown that acetone with a trace of acetic acid was a better solvent than acetic acid alone[3] for the initial potassium iodide reduction of the ozonide to 9-iodomethyl-10-methylanthracene. This product was shown by I.R. spectra to be identical with the material previously obtained by action of methylmagnesium iodide on anthraquinone, followed by HI reduction.[6]

Ozonation of 9-methoxy-10-methylanthracene (XI)

A solution of 0·935 g XI,[11] 30 ml acetone and 3 drops pyridine was ozonized at −78°. One mole of ozone was absorbed and a colourless, crystalline material precipitated. Attempts to collect the substance on a filter resulted in its decomposition to a yellow oil. In a separate experiment it was shown that 98% of the ozone ends up as active oxygen.

Ozonation of XI in methylene chloride using ozone-nitrogen, as described above for I, gave no precipitate of the ozonide. Determination of oxygen given off during the reaction[10] showed, within experimental error, that oxygen is not released during the ozonation. In a similar experiment using ozone-oxygen, a portion of the reaction mixture, kept at −78°, was used for the NMR probe.

Ozonation of 9-nitroanthracene[12]

A solution of 2 g 9-nitroanthracene in 200 ml methylene chloride was ozonized at −78°. Absorption of 2 mole-equivalents of ozone was quantitative, after which 2 more mole-equivalents were slowly absorbed. A solution of 200 ml water and 6 ml 90% hydrogen peroxide was added to the reaction mixture and the resulting solution was refluxed for several hours. A 16% yield of anthraquinone, identified by I.R. spectrum, subliming at 285°, was filtered off. The hydrogen peroxide in the filtrate was destroyed by addition of hydrochloric acid followed by refluxing. The resulting solution was continuously extracted with ether for 3 days. Evaporation of the ether extract gave a 75% yield of a water-soluble, pale yellow acid m.p. 212–215° (dec) after recrystallization from conc hydrochloric acid.[13] Paper chromatography showed the material to be pure. Found: C, 39·86; H, 1·87; N, 4·77[14]; Calc. for $C_{10}H_5NO_{10}$: C, 40·15; H, 1·68; N, 4·68%).

Using as solvent methylene chloride–glacial acetic acid (9:1) almost identical results were obtained.

Ozonation of 9,10-dinitroanthracene[12]

The ozonation was carried out as in the previous experiment. Ozone absorption was very slow, but several mole-equivalents were absorbed, whether the solvent was methanol, methylene chloride or mixtures thereof. By the work-up procedure described in the preceding experiment, a mixture of starting and other materials was obtained.

Ozonation of 9,10-diphenylanthracene

A mixture of 1·1 g 9,10-diphenylanthracene and 100 ml methylene chloride was ozonized at −78° with an ozone–nitrogen mixture. Slightly over 2 mole-equivalents of ozone were absorbed and one

[10] P. S. Bailey and A. M. Reader, *Chem. & Ind.* 1063 (1961).

[11] K. H. Meyer and H. Schlösser, *Liebigs Ann.* **420**, 130 (1920).

[12] This was carried out by Dr. F. Dobinson.

[13] E. Phillipi, *Liebigs Ann.* **428**, 286 (1922) reports 208° (dec) for nitropyromellitic acid.

[14] Performed by Alfred Bernhardt, Mülheim, Ruhr, Germany.

mole-equivalent of oxygen was evolved.[10] Titration of the reaction mixture showed that only 20% of the ozone ended up as active oxygen. Evaporation of the reaction mixture and chromatography of the residue over alumina gave only an oily mixture of products.

Ozonation of 9-phenylanthracene[15]

This was carried out in acetic acid at 13° with the absorption of 2–2·5 mole-equivalents of ozone The reaction mixture was evaporated and an essentially non-peroxidic, partially base-soluble resin was obtained. The material partially crystallized from acetic acid and, after several fractional recrystallizations, very low yields of anthraquinone (m.p. 270–274°, subl) and of 10-phenyl-10-hydroxyanthrone (m.p. 217–218°)[16] were obtained.

Found: C, 83·91; H, 6·19[17]; Calc. for $C_{20}H_{14}O_2$: C, 83·89; 4·93%).

By an oxidative work-up procedure (H_2O_2) a low yield of anthraquinone was obtained as the only crystalline product.

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[15] Carried out by Dr. J. B. Ashton.

[16] E. de B. Barnett and J. W. Cook, *J. Chem. Soc.* **123**, 2631 (1923) report 213–214°.

[17] Performed by the Biochemical Institute Microanalytical Laboratory, The University of Texas.