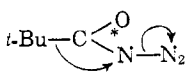
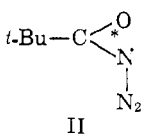
imidoyl azides (such as the N-phenylbenzimdoylazide presumably formed in the thermolysis of 1,5-diphenyltetrazole) thermolyze to a mixture of benzimidazoles (intramolecular nitrene cyclization) and carbodiimides (an "imido-Curtius rearrangement"). This might very well be a case were an imidoylnitrene both rearranges and cyclizes.

Establishing the existence of two parallel mechanisms in the photolysis of pivaloyl azide raises the question of the detailed nature. The nitrene formation most likely involves excitation of the azide to the lowest singlet excited state, followed by loss of nitrogen. The rearrangement might occur, simultaneous with the loss of nitrogen, in that same electronically excited state of the azide, perhaps in those molecules that happen to be in a more suitable conformation I rather than II.



I



II

Another possibility is a competition between the dissociation of the excited azide (to give nitrene) and its internal conversion to a highly vibrationally excited molecule. The latter would either be quenched by collisions, or undergo normal, thermal, Curtius rearrangement. The photoinduced rearrangement would, then, involve only a special route to vibrationally activated azide (in a cool environment). Both intimate mechanisms would, of course, be in accord with the mechanism of scheme 3.

## Experimental Section

The general techniques, authentic compounds, and pivaloyl azide have been described in the preceding paper.[15] Solvents and solvent mixtures used for the experiments were saturated with nitrogen; the cyclohexene was purified as before.[15]

***t*-Butyl isocyanate** was prepared, in 58% yield, by heating ethyl N-*t*-butylcarbamate[20] with powdered calcium hydroxide to 220°.[21] The thermal Curtius rearrangement of pivaloyl azide also gave pure *t*-butyl isocyanate.

**N-*n*-Butyl-N′-*t*-butylurea** was made by adding a solution of 1.46 g (0.2 mole) of *n*-butylamine in 10 ml of pentane to a solution of 1.98 g (0.2 mole) of *t*-butyl isocyanate in 10 ml of pentane, with cooling. An exothermic reaction occurred immediately. After 2 hr at room temperature, the solvent was removed. An almost quantitative yield of the urea crystallized upon refrigeration, mp 71–72°; infrared spectrum: NH at 3345 $cm^{-1}$ (broad), CO at 1631 $cm^{-1}$ (in $CCl_4$).

*Anal.* Calcd for $C_9H_{20}N_2O$: C, 62.75; H, 11.70; N, 16.26. Found: C, 62.66; H, 11.66; N, 16.14.

**Photolyses** were carried out, and the product yields determined as before.[15] The yields of *t*-butyl isocyanate were measured in a separate aliquot of the reaction mixtures by injecting 3 ml of *n*-butylamine at −10°. After 2 hr at −10°, and 1 hr at room temperature, the solvent was removed *in vacuo*. The residue was transferred to a 10-ml volumetric flask, and diluted to 10 ml with tetrahydrofuran. Vpc analyses were done on columns[15] A (160° column temperature) and B (146° column temperature).

**Photolysis in Benzene.** The photolysis was carried out as before[15] but since pure benzene would have frozen, a mixture of 45 ml of benzene and 5 ml of dichloromethane was used. During irradiation, the mixture turned light yellow. After evaporation of excess solvent and *t*-butyl isocyanate, an oily, nonvolatile residue remained. Its infrared spectrum (in $CCl_4$) showed absorptions at 3284, 2985, 1681, 1479, 1393, 1366, 1279, and 1242 $cm^{-1}$. The spectrum showed three multiplets at $\delta$ 1.25, 2.0, and 3.67.

**Acknowledgment.** We are greatly indebted to the National Science Foundation for generous support of this work.

(20) H. van Erp, *Rec. Trav. Chim.*, **14**, 17 (1895).
(21) B. Brauner, *Ber.*, **12**, 1874 (1879).

# Unsaturated Macrocyclic Compounds. LI.[1] 1,6-Oxido[10]annulene[2]

**Arnon Shani and Franz Sondheimer**[3]

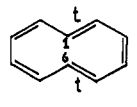
*Contribution from the Daniel Sieff Research Institute, the Weizmann Institute of Science, Rehovoth, Israel.* *Received June 19, 1967*

**Abstract:** 9,10-Oxido-1,4,5,8,9,10-hexahydronaphthalene (**10**) on hydrolysis to 1,4,5,8,9,10-hexahydronaphthalene-*trans*-9,10-diol (**11**), followed by successive bromination and dehydrobromination, gives the tribromo oxide **13a** and the diene bromo oxide **14** instead of the anticipated 9,10-dihydronaphthalene-*trans*-9,10-diol (**5**). The oxide **10** on bromination and subsequent dehydrobromination yields 1,6-oxido[10]annulene (**20**), as well as 1-benzoxepin (**24**). In agreement with theory, the ten $\pi$-electron system **20** is shown to be an aromatic compound. Various reactions of **20** are described, including its nitration to the 2- and 3-nitro derivatives **27** and **26**. 1,6-Oxido[10]annulene (**20**) is easily converted to naphthalene derivatives, *e.g.*, by lithium aluminum hydride reduction, catalytic hydrogenation, and treatment with acids.

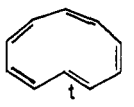
A variety of annulenes (monocyclic conjugated polyenes) and dehydroannulenes (monocyclic conjugated polyenynes) have been prepared in recent years.[4] These substances are expected to be aromatic, provided they contain $(4n + 2)$ out-of-plane $\pi$ electrons, the carbon skeleton is reasonably coplanar, and the ring size is below a certain limit.[4]

(1) For Part L, see C. C. Leznoff and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 4247 (1967).
(2) Taken from the Ph.D. thesis of A. Shani, Weizmann Institute of Science, March 1965.
(3) Author to whom inquiries may be addressed at the Chemistry Department, University College, London, W.C. 1, England.
(4) For reviews, see F. Sondheimer, *Pure Appl. Chem.*, 7, 363 (1963); F. Sondheimer, *Proc. Roy. Soc.* (London), **A297**, 173 (1967); F. Sondheimer, *et al.*, Special Publication No. 21, The Chemical Society, London, 1967, p 75.

Excepting for very large rings, the only series in which unbridged conjugated members have not been isolated is the ten-membered one. A number of groups, including our own, have been interested in the synthesis of [10]annulene (**1**, **2**, or **3**) and 1,6-bisdehydro[10]annulene (**4**).[5] These substances might be aromatic, since they contain $(4n + 2)$ out-of-plane $\pi$ electrons ($n = 2$), but in the case of [10]annulene steric or strain effects may cause destabilization. In practice, van Tamelen and Burkoth[6] very recently have obtained evidence that [10]annulene is formed as a




1

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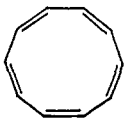

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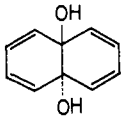
4

very unstable intermediate in the photolysis of *trans*-9,10-dihydronaphthalene.

The steric interaction of the two internal protons in **1** may be avoided by forming a bridge between C-1 and C-6. Such 1,6-bridged [10]annulenes have been prepared independently by E. Vogel, *et al.*, and by ourselves, as announced in preliminary communications.[7,8] Our own work, which has led to 1,6-oxido[10]annulene (**20**), is now reported in full.

Our original aim was the synthesis of 9,10-dihydronaphthalene-*trans*-9,10-diol (**5**). Cleavage of the 1,2-diol grouping in this substance with lead tetraacetate[9] or periodic acid was expected to lead to 2,4,7,9-cyclodecatetraene-1,6-dione ("[10]annulene quinone") (**6**), which on reduction might have given [10]annulene-1,6-diol (**7**).

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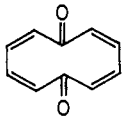


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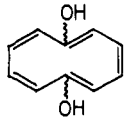
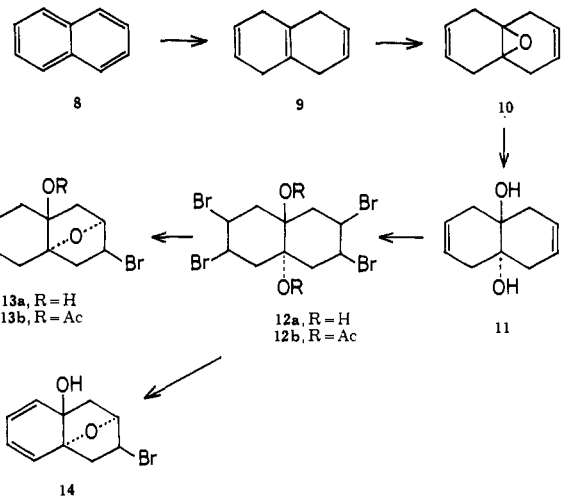



7

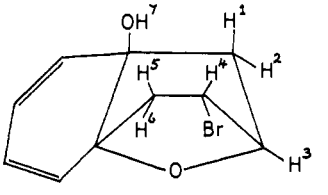
The starting material was 1,4,5,8,9,10-hexahydronaphthalene-*trans*-9,10-diol (**11**), which can be prepared readily in *ca.* 70% over-all yield from naphthalene (**8**) by reduction with sodium in liquid ammonia to 1,4,5,8-tetrahydronaphthalene (**9**),[10,11] followed by perbenzoic acid oxidation to 9,10-oxido-1,4,5,8,9,10-hexahydronaphthalene (**10**),[10-12] and subsequent treatment with aqueous acetic acid.[10,11] It was expected that **11**




might then be converted to the corresponding tetraene-diol **5** by a bromination–dehydrobromination sequence.

In the event, treatment of **11** with 2 molar equiv of bromine gave the tetrabromide **12a** in *ca.* 85% yield, apparently as one pure stereoisomer.[13] Substance **12a** could be converted to the corresponding diacetate **12b** by treatment with acetic anhydride and boron trifluoride. A number of dehydrobromination experiments were carried out with **12a** and **12b** with several different bases (potassium *t*-butoxide, potassium hydroxide, sodamide, etc.) under various conditions. However, the required tetraene diol **5** did not appear to be formed in any case. The results obtained by treatment of **12a** with potassium *t*-butoxide are typical. Use of a considerable excess of this base in *t*-butyl alcohol and dioxane at 60° gave the diene oxide **14** in *ca.* 20% yield as the only substance to be isolated. Treatment of **12a** with only 2 molar equiv of potassium *t*-butoxide under these conditions led to 30% of the tribromo oxide **13a** in addition to 5% of **14**, and **13a** is therefore presumably an intermediate in the dehydrobromination of **12a** to **14**. Interestingly, the tribromo oxide **13a** was also obtained from **12a** (in 25% yield) by attempted glycol cleavage with lead tetraacetate and trichloroacetic acid in acetic acid.

Both the ethers **13a** and **14** must possess one ring in the boat form. The structure of the diene bromo oxide **14** was based on the elemental composition, the ultraviolet spectrum [$\lambda_{max}^{EtOH}$ 256 mμ (ε 3900)],[14] and the nmr spectrum. The latter showed a four-proton multiplet (olefinic protons) at τ 3.32–4.00, a 1-proton doublet ($H^4$; see formula A) at τ 5.43 ($J_{H^4H^5}$ = 6 cps),




A

(5) See T. J. Sworski, *J. Chem. Phys.*, **16**, 550 (1948).

(6) E. E. van Tamelen and T. L. Burkoth, *J. Am. Chem. Soc.*, **89**, 151 (1967).

(7) (a) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964); (b) E. Vogel, N. Biskup, W. Pretzer, and W. A. Böll, *ibid.*, **76**, 785 (1964); (c) E. Vogel, W. Pretzer, and W. A. Böll, *Tetrahedron Letters*, 3613 (1965); (d) E. Vogel, W. Grimme, and S. Korte, *ibid.*, 3625 (1965); (e) E. Vogel, F. Weyres, H. Lepper, and V. Rautenstrauch, *Angew. Chem.*, **78**, 754 (1966).

(8) F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964).

(9) The lead tetraacetate cleavage of the related 1,4,5,8,9,10-hexahydronaphthalene-*trans*-9,10-diol (**11**) had already been reported.[10]

(10) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960).

(11) W. Hückel and H. Schlee, *Chem. Ber.*, **88**, 346 (1955).

(12) In our hands, the oxidation of **9** to **10** was carried out most conveniently with *m*-chloroperbenzoic acid (see Experimental Section).

(13) The stereochemistry of the bromo substituents in **12a** and the other bromo compounds is unknown, and the solid lines joining these substituents to the rings in the corresponding formulas have no stereochemical significance.

(14) 1,3-Cyclohexadiene exhibits $\lambda_{max}^{hexane}$ 256 mμ (ε 7900),[15] while steroidal 1,3-dienes (in which a 1,3-cyclohexadiene ring is *trans*-fused to a cyclohexane ring, as in **14**) show $\lambda_{max}^{EtOH}$ 262 mμ (ε 3800).[16]

(15) V. Henri and L. W. Pickett, *J. Chem. Phys.*, 7, 439 (1939).

(16) B. Berkoz, A. D. Cross, M. E. Adame, H. Carpio, and A. Bowers, *J. Org. Chem.*, **28**, 1976 (1963).

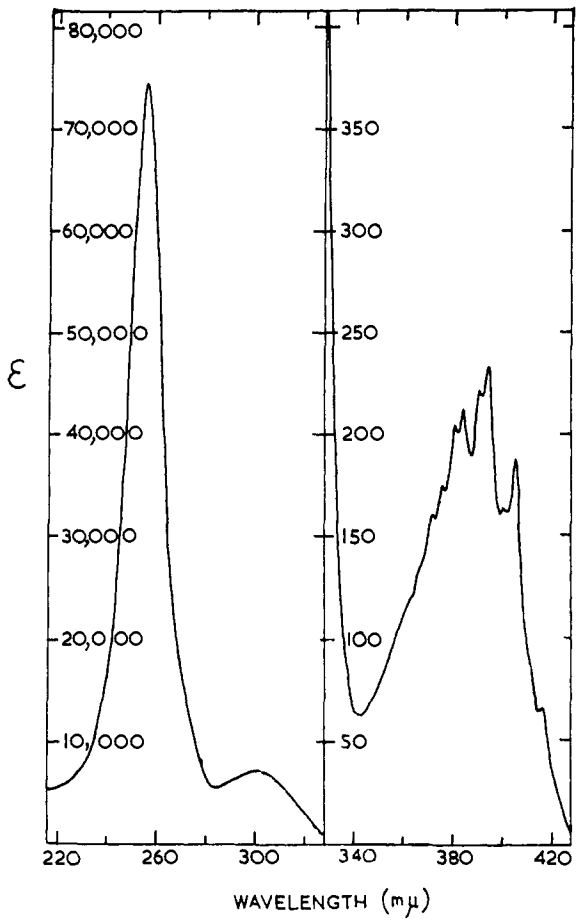
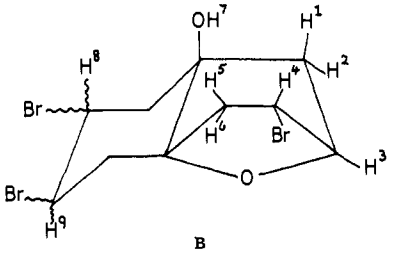



Figure 1. Ultraviolet absorption spectrum of 1,6-oxido[10]annulene (**20**) measured in ethanol with a Cary Model 14 spectrometer.

a one-proton double doublet ($H^3$) at $\tau$ 5.64 ($J_{H^3H^1}$ = 8 cps, $J_{H^3H^2}$ = 4 cps), a one-proton double doublet ($H^1$) at $\tau$ 6.60 ($J_{H^1H^2}$ = 14 cps, $J_{H^1H^3}$ = 8 cps), and a four-proton complex band ($H^2$, $H^5$, $H^6$, $H^7$) at $\tau$ 7.50–8.48.

The tribromo oxide **13a** exhibited no appreciable absorption in the ultraviolet. The lack of unsaturation was confirmed by the facts that no color was produced with tetranitromethane, no hydrogen was absorbed on attempted catalytic hydrogenation over a platinum catalyst, and there were no olefinic proton bands in the nmr spectrum. The latter showed a three-proton multiplet ($H^4$, $H^8$, $H^9$; see formula B) at $\tau$ 5.00–5.40,



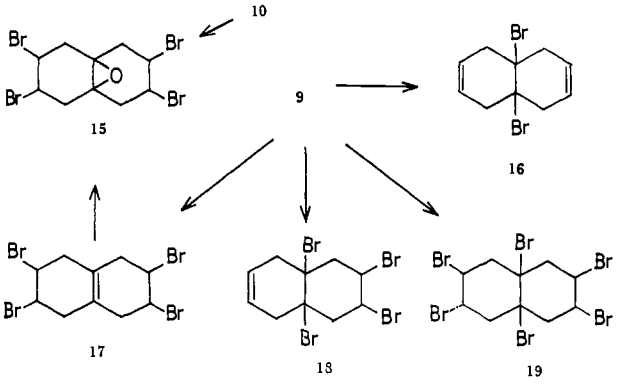

B

a one-proton double doublet ($H^3$) at $\tau$ 5.72 ($J_{H^3H^1}$ = 8 cps, $J_{H^3H^2}$ = 4 cps), a one-proton double doublet ($H^1$) at $\tau$ 6.70 ($J_{H^1H^2}$ = 14 cps, $J_{H^1H^3}$ = 8 cps), a one-proton singlet ($H^7$, disappears on addition of $D_2O$) at $\tau$ 6.91, and a seven-proton complex band (remaining protons) at $\tau$ 6.80–8.55.

Treatment of the tribromo oxide **13a** with acetic anhydride and boron trifluoride gave the acetate **13b**. The nmr spectrum of this acetate was similar to that of the corresponding alcohol **13a**, except that the hydroxyl proton band ($H^7$ in B) at $\tau$ 6.91 had been replaced by a three-proton singlet at $\tau$ 7.90 due to the acetate methyl group.

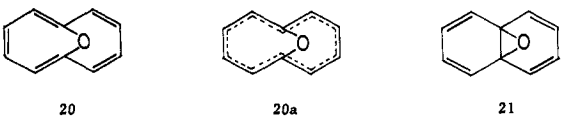
Evidently, the presence of the hydroxyl groups in the tetrabromodiol **12a** was responsible for the observed ether formation, rather than the desired tetradehydrobromination to the tetraenediol **5**. It was therefore decided to reverse the order of steps, by carrying out the bromination–dehydrobromination sequence with the diene oxide **10**.

Treatment of **10** with 2 molar equiv of bromine led to the tetrabromo oxide **15** as a stereoisomeric mixture, from which an apparently pure isomer could be sep-




arated in *ca.* 40% yield by crystallization. The same isomer of **15** could also be obtained, though only in very poor yield, by the following route. Bromination of 1,4,5,8-tetrahydronaphthalene (**9**) with 2 molar equiv of bromine gave mainly the 9,10-dibromide **16** (*ca.* 60%), as well as smaller amounts of the 2,3,6,7-tetrabromide **17** (*ca.* 5%), the 2,3,9,10-tetrabromide **18** (*ca.* 5%), and the 2,3,6,7,9,10-hexabromide **19** (*ca.* 10%). The structures assigned to the bromo compounds are based on the elemental analyses and the nmr spectra. Oxidation of the 2,3,6,7-tetrabromide **17** with perbenzoic acid in chloroform for 2 weeks then led (in *ca.* 10% yield) to the same isomer of the tetrabromo oxide **15** as obtained previously.

Dehydrobromination of the tetrabromo oxide **15** (pure isomer) with a large excess of potassium hydroxide in ethanol at 50–55° gave two substances, separated by chromatography on alumina. The major product (yellow crystals, 50% yield) proved to be 1,6-oxido-[10]annulene (**20**), while the minor one (yellow liquid, 20% yield) was 1-benzoxepin (**24**).

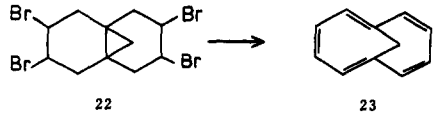



20 20a 21

The ultraviolet and nmr spectra of the crystalline product clearly pointed to the bicyclic 1,6-oxido[10]-annulene structure (**20**) rather than to the tricyclic 9,10-oxido-9,10-dihydronaphthalene structure (**21**). The ultraviolet spectrum [$\lambda_{max}^{EtOH}$ 255, 299, and complex band at *ca.* 393 mμ (ε 74,000, 6900, and 240, respectively) (Figure 1)] was consistent with the fully conjugated formulation **20**, whereas **21** should have exhibited the 1,3-cyclohexadiene type of spectrum shown by **14**. The nmr spectrum (Figure 2) showed an $A_2B_2$ pattern in the

$\tau$ 2.23–2.81 region (centered at $\tau$ 2.52), similar to that of naphthalene ($\tau$ 2.05–2.71, centered at $\tau$ 2.38). The low-field position of the nmr signals indicated the existence of a diamagnetic ring current,[4] as expected for the ten-$\pi$-electron system **20**, but not for the oxide **21**. 1,6-Oxido[10]annulene is best represented by formula **20a**, indicating delocalization of the $\pi$ electrons.

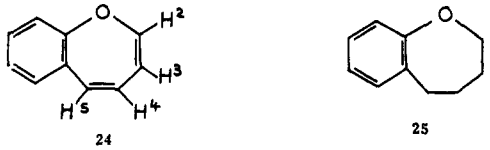
While the above-described work was in progress, Vogel and Roth[7a] reported the synthesis of the closely related 1,6-methano[10]annulene (**23**) by dehydro-




22 23

bromination of the tetrabromide **22**. As expected, **20** and **23** exhibited similar ultraviolet and nmr spectra, confirming the structural relationship.

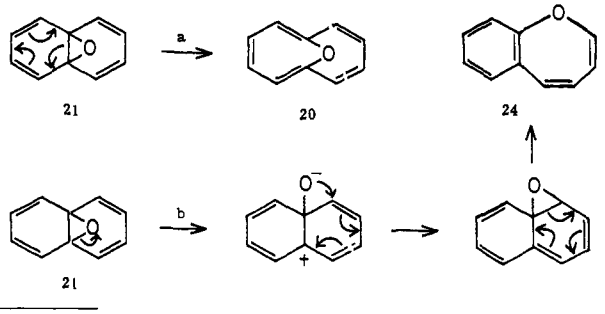
The 1-benzoxepin structure **24**[17] was assigned to the liquid dehydrobromination product on the basis of the nmr spectrum. This consisted of a four-proton




24 25

multiplet (benzenoid protons) at *ca.* $\tau$ 2.5–3.2, a one-proton doublet ($H^5$) at $\tau$ 3.37 ($J_{H^5H^4}$ = 11 cps), a one-proton doublet ($H^2$) at $\tau$ 3.79 ($J_{H^2H^3}$ = 5.5 cps), a one-proton double doublet ($H^4$) at $\tau$ 4.03 ($J_{H^4H^5}$ = 5.5 cps, $J_{H^4H^3}$ = 11 cps), and a one-proton double doublet ($H^3$) at $\tau$ 4.60 ($J_{H^3H^2}$ and $J_{H^3H^4}$ = 5.5 cps). Confirmation of this structure was provided by catalytic hydrogenation in pentane over palladium–charcoal to the known 2,3,4,5-tetrahydro-1-benzoxepin (homochroman) (**25**), identified by direct comparison with an authentic sample.[19]

The formation of 1,6-oxido[10]annulene (**20**) and 1-benzoxepin (**24**) from the tetrabromide **15** can easily be rationalized. Dehydrobromination of **15** presumably leads first to the tetraene oxide **21**, which may give rise to **20** by path a and **24** by path b. It could be shown that the two products **20** and **24** are formed by




21 20 24

21

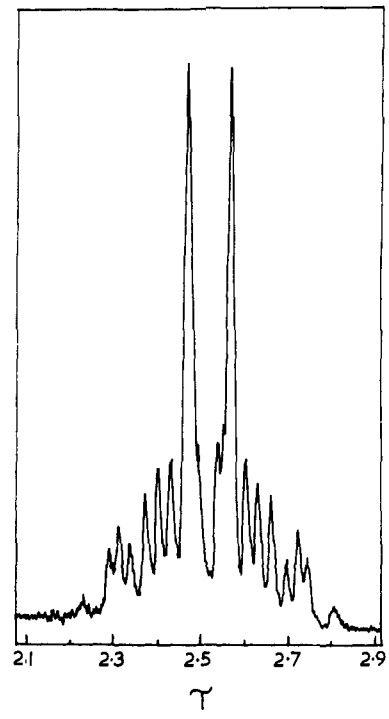



Figure 2. Nmr spectrum of 1,6-oxido[10]annulene (**20**) measured in deuteriochloroform with a Varian A-60 spectrometer (tetramethylsilane used as internal reference).

independent routes, since each was recovered unchanged on base treatment under the conditions used for its formation. Alkaline alumina also caused no change.

On the other hand, 1,6-oxido[10]annulene (**20**) was unstable under acidic conditions. Treatment with acid-washed alumina or with silica gel for several hours caused rearrangement to 1-benzoxepin (**24**) in at least 50% yield, and small amounts (*ca.* 2.5%) of $\alpha$-naphthol were also isolated. Reaction of **20** with boron trifluoride etherate in chloroform at room temperature gave the same two products, but under these conditions $\alpha$-naphthol was the major product (70%) and 1-benzoxepin the minor one (2%). Treatment of **20** with aqueous acetic acid at 50° led to a *ca.* 1:1 mixture of $\alpha$- and $\beta$-naphthol in 50% yield, as well as to 25% of 1-benzoxepin (**24**). It is of interest that 1-benzoxepin (**24**) was also rearranged with acids, being converted to $\alpha$-naphthol (in poor yield) by means of concentrated sulfuric acid or with boron trifluoride etherate in chloroform.[20] Several mechanisms can be considered which account for the observed rearrangements. No clear distinction between them can be made without further work (*e.g.*, determining whether the oxygen atom in the rearrangement products is the same as in the starting material, or is derived from outside sources), and further discussion is therefore not justified at this stage.

Catalytic hydrogenation of 1,6-oxido[10]annulene (**20**) in pentane over palladium–charcoal for several hours led to tetralin in *ca.* 95% yield. This substance must have been formed *via* naphthalene, since naphthalene was isolated in excellent yield when the hydrogenation (in ethanol) was terminated after 5 min. Sim-

(17) The isomeric 3-benzoxepin[18a] and its derivatives[18b–e] have been reported previously. Derivatives of 1-benzoxepin,[18f] as well as 2,7-dimethyloxepin[18g] and oxepin itself,[18h] have now been prepared.

(18) (a) K. Dimroth and G. Pohl, *Angew. Chem.*, **73**, 436 (1961); (b) K. Dimroth and H. Freyschlag, *Ber.*, **90**, 1623 (1957); (c) R. Huisgen, E. Laschtuvka, I. Ugi, and A. Kammermeier, *Ann.*, **630**, 128 (1960); (d) F. Dallacker, K. W. Glombitza, and M. Lipp, *ibid.*, **643**, 82 (1961); (e) M. J. Jorgenson, *J. Org. Chem.*, 27, 3224 (1962); (f) H. Hofmann, *Angew. Chem.*, 77, 864 (1965); (g) E. Vogel, R. Schubart, and W. A. Böll, *ibid.*, 76, 535 (1964); (h) E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Letters*, 609 (1965).

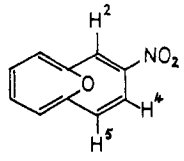
(19) G. Baddeley, N. H. P. Smith, and M. A. Vickars, *J. Chem. Soc.*, 2455 (1956).

(20) By comparison, the isomeric 3-benzoxepin is rearranged to 3-indenecarboxaldehyde on treatment with alcoholic hydrochloric acid.[18a]

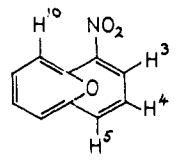
ilarly, reduction of **20** with lithium aluminum hydride gave naphthalene in high yield as sole product.

1,6-Oxido[10]annulene (**20**) is a ten-$\pi$-electron system, presumably with a reasonably planar carbon skeleton,[21] and it should therefore be aromatic.[4] In agreement with this expectation is the above-mentioned nmr spectrum. It was of interest to investigate whether **20** was aromatic also in the classical sense, and electrophilic substitution reactions were therefore studied.

Nitration of 1,6-oxido[10]annulene (**20**) with cupric nitrate in acetic anhydride at room temperature[22] led to two mononitro compounds, each in *ca.* 30% yield.[25] The more strongly absorbed on alumina (mp 48–49°) was assigned the 3-nitro structure **26**, as evidenced by the nmr spectrum. This spectrum consisted of a low-field one-proton singlet ($H^2$) at $\tau$ 1.22, and a




**26**



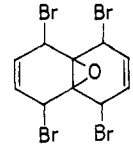

**27**

low-field one-proton doublet ($H^4$) at $\tau$ 1.40 ($J_{H^4H^5}$ = 10 cps); in addition, a five-proton complex band at $\tau$ 1.95–2.54 was apparent, assigned to the remaining protons. The less strongly absorbed nitro compound (mp 86–87°) was assigned the 2-nitro structure **27**. The nmr spectrum showed a two-proton low-field band, apparently consisting of a superimposed doublet ($H^3$) at $\tau$ 1.37 ($J_{H^3H^4}$ = 10 cps) and a doublet ($H^5$ or $H^{10}$) at *ca.* $\tau$ 1.48; in addition, a five-proton complex band at $\tau$ 1.94–2.64 was present, assigned to the remaining protons.

Attempts were made to reduce the two nitro compounds **26** and **27** to the corresponding amino compounds under various conditions, but no pure products could be isolated from these experiments.

It was not possible to effect other substitution reactions with **20**, due to the very ready formation of naphthalene derivatives. Thus, attempted acylation of **20** with acetic anhydride and boron trifluoride etherate in chloroform at room temperature[23,24] led to $\alpha$-naphthyl acetate in over 70% yield.[27] This was not unexpected, since it has already been found that treatment of **20** with boron trifluoride etherate in chloroform gives rise to $\alpha$-naphthol. Attempted sulfonation of **20** by means of oleum in dioxane at room temperature, followed by treatment with silver nitrate and then with methyl iodide,[23] yielded material exhibiting ultraviolet light absorption properties indicative of a naphthalene derivative. However, no pure substance could be isolated from this reaction.

Some experiments were carried out to investigate whether 1,6-oxido[10]annulene (**20**) would undergo addition reactions. Attempted Diels–Alder reaction with maleic anhydride in boiling benzene for 2 hr led to no significant change, confirming the aromatic character of the substance.[28] However, treatment of **20** with excess bromine in chloroform at room temperature gave rise to two substances (mp 156–158° and 153–155°) in *ca.* 65 and 10% yield, respectively, the elemental analyses of which showed each one to be derived from **20** by the addition of 2 molecules of bromine. The spectral data of these tetrabromides did not allow unique structural assignments to be made. However, the major one was subsequently found to be identical (infrared and nmr spectral comparison) with the tetrabromide (mp 152–153°) prepared from **20** by a two-step sequence by Vogel, *et al.*,[29] to which structure **28** has been assigned.




**28**

To summarize, 1,6-oxido[10]annulene (**20**) has been found to be an aromatic substance, both from a "modern" point of view (nmr spectrum) and a "classical" point of view (formation of nitro derivatives). However, the chemical transformations of the substance are complicated by the fact that it is easily transformed to naphthalene derivatives.

After the appearance of our preliminary communication[8] describing the synthesis of 1,6-oxido[10]annulene (**20**), Vogel, *et al.*,[7b] reported in preliminary form the independent synthesis of the same substance by a similar route. The dehydrobromination of the tetrabromide **15** was carried out with potassium *t*-butoxide in ether at −10°, whereby **20** was obtained in 60% yield, apparently unaccompanied by 1-benzoxepin (**24**) (**24** was formed by chromatography of **20** on silica gel). The properties and reactions of **20** described by this group[7b] in general are in good agreement with those found by us.[30]

Detailed analyses of the nmr[32] and electronic[33] spectra of 1,6-oxido[10]annulene (**20**) have now been reported. In addition, the esr spectrum of the radical

(21) The periphery of the related 1,6-methano[10]annulene-2-carboxylic acid has been shown to be not seriously distorted from a mean plane [M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 48, 1429 (1965)]. An X-ray crystallographic analysis of **20** is now being carried out by Professor R. Mason, Sheffield University. A preliminary account of this work has now been published [N. A. Bailey and R. Mason, *Chem. Commun.*, 1039 (1967)].

(22) These conditions have been used by our group for the nitration of conjugated 14-membered[23] and 18-membered[24] ring compounds.

(23) Y. Gaoni and F. Sondheimer, *J. Am. Chem. Soc.*, **86**, 521 (1964).

(24) I. C. Calder, P. J. Garratt, H. C. Longuet-Higgins, F. Sondheimer, and R. Wolovsky, *J. Chem. Soc., Sect. C*, 1041 (1967).

(25) Similarly, nitration of 1,6-methano[10]annulene (**23**) with cupric nitrate in acetic anhydride leads apparently to a mixture of the 2- and 3-nitro derivatives.[26]

(26) E. Vogel and W. A. Böll, *Angew. Chem.*, **76**, 784 (1964).

(27) By comparison, 1,6-methano[10]annulene (**23**) has been found to give the corresponding 2-acetyl compound on treatment with acetic anhydride and stannic chloride.[26]

(28) Similarly, Vogel and Böll[26] have found that 1,6-methano[10]-annulene (**23**) does not react with maleic anhydride in boiling benzene. However, it was shown that a 1:1 adduct is formed when this reaction is carried out in boiling chlorobenzene for several hours, the product being derived from the tricyclic norcaradiene isomer of compound **23** [E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Letters*, 3625 (1965)].

(29) E. Vogel, W. A. Böll, and M. Biskup, *ibid.*, 1569 (1966).

(30) The only significant difference appears to be the fact that the 3-nitro compound **26** (obtained, together with the 2-nitro isomer **27**, by Vogel, *et al.*,[31] by the nitration of **20** with cupric nitrate in acetic anhydride) showed mp 60–61°, whereas our sample exhibited mp 48–49°. The nmr and infrared spectra of both samples of **26** were found to be identical by direct comparison (as were the nmr and infrared spectra of **27**), and the difference in melting point may be due to polymorphism.

(31) E. Vogel, private communication.

(32) H. Günther, *Z. Naturforsch.*, 20b, 948 (1965).

(33) H. R. Blattmann, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel, and J. P. Weber, *Helv. Chim. Acta*, **49**, 2017 (1966).

anion of (**20**) (as well as of 2,5,7,10-tetradeuterio-1,6-oxido[10]annulene obtained from **20** by treatment with potassium *t*-butoxide in perdeuteriodimethyl sulfoxide) has been determined.[34] All these spectra confirm the aromatic nature of **20**.[35]

## Experimental Section[36]

**9,10-Oxido-1,4,5,8,9,10-hexahydronaphthalene (10).** 1,4,5,8-Tetrahydronaphthalene (**9**) (mp 55–57°; obtained in *ca.* 85% yield by sodium–ammonia reduction of naphthalene)[10,11] on oxidation with perbenzoic acid (1 molar equiv) in chloroform[10,11] led to the oxide **10** (mp 58–60°) in *ca.* 75% yield.

The oxidation of **9** to **10** was subsequently carried out most conveniently with *m*-chloroperbenzoic acid (experiments by K. Grohmann and P. J. Mulligan). A solution of *m*-chloroperbenzoic acid (185 g, 85% pure, 0.91 mole) in chloroform (3 l.) was added during 1.5 hr to a stirred solution of **9** (119 g, 0.90 mole) in chloroform (400 ml), the internal temperature being kept between −5 and 5° by ice–salt cooling. The suspension was stirred at *ca.* 5° for a further 30 min, and a solution of sodium hydroxide (44 g, 1.1 moles) in water (1 l.) was then added during 5 min, with continued cooling and vigorous stirring. The chloroform layer was separated, washed with water, and dried over potassium carbonate. Evaporation under reduced pressure and crystallization from petroleum ether (bp 40–60°) led to **10** (101.5 g, 76%), mp 60–62°.

**1,4,5,8,9,10-Hexahydronaphthalene-*trans*-9,10-diol (11).** The diol **11** (mp 81–83°) was prepared by treatment of the crude uncrystallized oxide **10** with dilute acetic acid, according to Grob and Schiess.[10] The over-all yield from naphthalene was *ca.* 70%, both when **10** was prepared with perbenzoic acid and with *m*-chloroperbenzoic acid.

**2,3,6,7-Tetrabromodecahydronaphthalene-*trans*-9,10-diol (12a) and Diacetate (12b).** A solution of bromine (11.2 g, 0.07 mole) in chloroform (30 ml) was added dropwise during 30 min to a stirred solution of the diol **11** (5.8 g, 0.035 mole) in chloroform (100 ml), the internal temperature being kept at 5–10° by ice cooling. The mixture was stirred at this temperature for a further 30 min, and the resulting precipitate, consisting of the tetrabromo diol **12a** (12.95 g, mp 208–210°), was collected. The filtrate, on being washed with sodium sulfite solution, dried, and evaporated, afforded a further 1.25 g of **12a**, mp 204–208° (total yield, 14.20 g, 84%). Crystallization from chloroform–ethanol gave a sample: mp 210–212°; $\lambda_{max}^{KBr}$ 2.76, 7.02, 7.36, 8.18, 8.35, 9.56, 10.16, 11.26, and 11.73 μ.

*Anal.* Calcd for $C_{10}H_{14}Br_4O_2$: C, 24.72; H, 2.90; Br, 65.79. Found: C, 24.90; H, 2.70; Br, 65.49.

The diacetate **12b** was prepared by adding boron trifluoride etherate (20 drops) to a suspension of the tetrabromo diol **12a** (90 mg) in acetic anhydride (15 ml), warming the mixture to *ca.* 45° for 5 min, and then allowing it to stand at room temperature for 24 hr. The resulting **12b** (48 mg, mp 256–257°) was collected. The mother liquors afforded a further 13 mg, mp 252–253° (total yield, 61 mg, 58%) by addition of water and extraction with chloroform. After recrystallization from chloroform, **12b** showed mp 258–259°; $\lambda_{max}^{KBr}$ 5.72, 7.01, 7.35, 8.22, 8.38, 9.53, 10.21, 11.29, and 12.30 μ.

*Anal.* Calcd for $C_{14}H_{18}Br_4O_4$: C, 29.50; H, 3.18; Br, 56.09. Found: C, 29.12; H, 3.14; Br, 55.80.

**Dehydrobromination of 12a to 2,10-Oxido-3,6,7-tribromo-*trans*-decahydronaphthalen-9-ol (13a) and 2,10-Oxido-3-bromo-*trans*-1,2,-3,4,9,10-hexahydronaphthalen-9-ol (14). a. With 2 Molar Equiv of Potassium *t*-Butoxide.** A solution prepared by dissolving potassium (390 mg, 10 mmoles) in dry *t*-butyl alcohol (80 ml) and diluting with dry dioxane (20 ml) was added to a suspension of the tetrabromo diol **12a** (2.43 g, 5 mmoles) in dioxane (50 ml). The stirred mixture was heated for 1 hr at 60°, and was then evaporated to small volume under reduced pressure. Isolation with ether led to a mixture, which was chromatographed on alumina (100 g, Alcoa F-20). Elution with pentane–ether (9:1) gave the tribromo oxide **13a** (590 mg, 29%), which separated from petroleum ether (bp 40–60°) as crystals: mp 123–124°; $\lambda_{max}^{KBr}$ 2.74, 7.08, 8.18, 8.49, 9.21, 9.33, 9.72, 10.12, 10.46, 11.51, 12.25, 12.98, and 14.56 μ; no appreciable ultraviolet absorption; nmr spectrum, see Discussion.

*Anal.* Calcd for $C_{10}H_{13}Br_3O_2$: C, 29.66; H, 3.24; Br, 59.20. Found: C, 29.85; H, 3.06; Br, 58.87.

Further elution with pentane–ether (4:1) yielded the diene bromo oxide **14** (55 mg, 4.5%), which separated from petroleum ether (bp 40–60°) as crystals: mp 100–101°; $\lambda_{max}^{KBr}$ 2.85, 8.16, 9.30, 10.15, 10.25, 10.33, 11.02, 12.25, 12.60, and 13.95 μ; $\lambda_{max}^{EtOH}$ 256 mμ (ε 3900); nmr spectrum, see Discussion.

*Anal.* Calcd for $C_{10}H_{11}BrO_2$: C, 49.40; H, 4.56; Br, 32.87. Found: C, 49.78; H, 4.79; Br, 33.20.

Several repetitions of this experiment resulted in variable yields of **13a** and **14**.

**b. With Excess Potassium *t*-Butoxide (Experiment by P. J. Mulligan).** The dehydrobromination of the tetrabromodiol **12a** (2.43 g, 5 mmoles) was carried out as described under a, except that an excess of potassium *t*-butoxide (prepared from potassium (980 mg, 25 mg-atoms) and *t*-butyl alcohol (100 ml)) was used. Chromatography on alumina (100 g, Spence type H), elution with pentane–ether (1:9), and crystallization from petroleum ether (bp 40–60°), yielded the diene bromo oxide **14** (233 mg, 19%), mp 98–100°. No tribromo oxide **13a** was isolated.

**2,10-Oxido-3,6,7-tribromo-*trans*-decahydronaphthalen-9-ol Acetate (13b).** The tribromo oxide **13a** (140 mg) in acetic anhydride (10 ml) containing boron trifluoride etherate (five drops) was allowed to stand at room temperature for 16 hr. Isolation with ether and crystallization from chloroform–petroleum ether (bp 40–60°) gave the acetate **13b** (115 mg, 74%): mp 134–135°; $\lambda_{max}^{KBr}$ 5.75, 7.32, 8.04, 8.50, 9.38, 9.62, 10.24, 10.38, 11.66, 12.30, and 14.98 μ: no appreciable ultraviolet absorption; nmr spectrum (for numbering, see formula B), three-proton multiplet ($H^4$, $H^8$, $H^9$) at τ 5.17–5.47, one-proton double doublet ($H^3$) at τ 5.82 ($J_{H^3H^1}$ = 8 cps, $J_{H^3H^2}$ = 5 cps), one-proton double doublet ($H^1$) at τ 6.83 ($J_{H^1H^2}$ = 15 cps, $J_{H^1H^3}$ = 8 cps), three-proton singlet (acetate methyl protons) at τ 7.90, and seven-proton complex band (remaining protons) at τ 6.80–8.40.

*Anal.* Calcd for $C_{12}H_{15}Br_3O_3$: C, 32.24; H, 3.38; Br, 53.64. Found: C, 32.64; H, 3.21; Br, 54.04.

**2,10-Oxido-3,6,7-tribromo-*trans*-decahydronaphthalen-9-ol (13a) by Treatment of 12a with Lead Tetraacetate.** Trichloroacetic acid (1.0 g, 6.1 mmoles) and lead tetraacetate (3.4 g, 7.7 mmoles) were added to a solution of the tetrabromo diol **12a** (2.43 g, 5 mmoles) in acetic acid (100 ml), and the mixture was heated at 100° for 2 hr. The product was isolated with ether and chromatographed on alumina (50 g, Merck, acid washed). Elution with pentane–ether (19:1) and crystallization from petroleum ether (bp 40–60°) yielded the tribromo oxide **13a** (505 mg, 25%), mp 123–124°, identified with the above-described material by mixture melting point determination and infrared spectral comparison.

Elution with pentane–ether (9:1) and crystallization from petroleum ether (bp 40–60°) gave an isomer of **13a** (40 mg, 2%): mp 159–160°; $\lambda_{max}^{KBr}$ 2.85, 6.95, 7.65, 8.16, 8.48, 8.85, 9.08, 9.27, 9.62, 9.92, 10.36, 10.69, 10.86, 11.53, 11.66, 12.09, 12.38, 13.12, and 14.34 μ.

*Anal.* Calcd for $C_{10}H_{13}Br_3O_2$: C, 29.66; H, 3.24; Br, 59.20. Found: C, 30.14; H, 2.88; Br, 58.67.

Mainly starting material was obtained when the reaction was carried out with lead tetraacetate and trichloroacetic acid in methanol at room temperature (conditions of Grob and Schiess[10]) or at reflux temperature for 1 hr. Similarly, no appreciable reaction occurred when **12a** was treated with excess periodic acid in aqueous dioxane for 6 hr.

**Bromination of 1,4,5,8-Tetrahydronaphthalene (9).** A solution of bromine (16.0 g, 0.1 mole) in chloroform (50 ml) was added dropwise during 30 min to a stirred solution of **9** (6.6 g, 0.05 mole) in chloroform (50 ml), the internal temperature being kept at 10–15° by ice cooling. The mixture was stirred at this temperature for a further 30 min, and the resulting precipitate was collected. It consisted of the very insoluble 2,3,6,7,9,10-hexabromodecahydronaphthalene (**19**) (3.1 g, 10.1%): mp 281–285°; $\lambda_{max}^{KBr}$ 6.98, 7.47, 8.37, 8.55, 9.40, 10.63, 11.86, 13.36, and 14.44 μ.

*Anal.* Calcd for $C_{10}H_{12}Br_6$: C, 19.63; H, 1.98. Found: C, 19.88; H, 1.93.

(34) F. Gerson, E. Heilbronner, W. A. Böll, and E. Vogel, *Helv. Chim. Acta*, **48**, 1494 (1965).

(35) The dipole moment of 1,6-oxido[10]annulene has now also been reported [W. Bremser, H. T. Grunder, E. Heilbronner, and E. Vogel, *ibid.*, **50**, 84 (1967)].

(36) Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Unless otherwise stated, infrared spectra were determined with a Perkin-Elmer Model 137 Infracord spectrometer (only the main bands are given), ultraviolet spectra with a Cary Model 14 spectrometer, and nmr spectra with a Varian A-60 spectrometer (deuteriochloroform solutions, tetramethylsilane used as internal reference). Microanalyses were carried out in our microanalytical department under the direction of Mr. Raoul Heller.

The filtrate was washed with sodium sulfite solution, and was then dried and evaporated. Crystallization from chloroform–petroleum ether (bp 40–60°) afforded 2,3,6,7-tetrabromo-1,2,3,4,5,6,7,8-octahydronaphthalene (**17**) (1.31 g, 5.8%): mp 194–195°; $\lambda_{max}^{KBr}$ 7.05, 7.55, 8.07, 8.62, and 10.40 $\mu$; nmr spectrum (100 Mcps), four-proton singlet (protons on carbon bearing bromine) at $\tau$ 5.46, and two four-proton doublets (allylic protons) at $\tau$ 6.88 and 7.58 ($J$ = 18 cps).

*Anal.* Calcd for $C_{10}H_{12}Br_4$: C, 26.58; H, 2.68; Br, 70.74. Found: C, 26.99; H, 2.68; Br, 70.64.

Crystallization of the mother liquors from chloroform–petroleum ether (bp 40–60°) yielded 9,10-dibromo-1,4,5,8,9,10-hexahydronaphthalene (**16**) (8.7 g, 60%): mp 156–157°; $\lambda_{max}^{KBr}$ 6.00, 7.05, 7.46, 8.08, 9.01, 10.02, 10.26, 13.60, 14.61, and 14.96 $\mu$; nmr spectrum, four-proton singlet (olefinic protons) at $\tau$ 4.13, and eight-proton singlet (allylic protons) at $\tau$ 7.05.

*Anal.* Calcd for $C_{10}H_{12}Br_2$: C, 41.13; H, 4.14; Br, 54.73. Found: C, 41.03; H, 4.17; Br, 55.20.

In another experiment (carried out by P. J. Mulligan), bromine (267 g, 1.67 moles) in chloroform (500 ml) was added to a solution of **9** (110 g, 0.83 mole) in chloroform (750 ml) at 0–10° during 2 hr, and the mixture was stirred at this temperature for another 2 hr. The precipitated hexabromide **19** (54.5 g, 10.7%) was removed, and the filtrate was evaporated. Fractional crystallization of the residue from chloroform–pentane yielded the 2,3,6,7-tetrabromide **17** (16.4 g, 4.4%) and the 2,3,9,10-tetrabromide **18** (20.0 g, 5.3%); the residual dibromide **16** was not isolated in this case. 2,3,9,10-Tetrabromo-1,2,3,4,5,8,9,10-octahydronaphthalene (**18**) showed mp 155–157°; $\lambda_{max}^{KBr}$ (Perkin-Elmer Model 257) 6.05, 6.99, 7.50, 8.23, 8.47, 10.16, 10.44, 10.89, 12.18, 13.51, 14.34, and 15.08 $\mu$; nmr spectrum (100 Mcps), two-protons inglet (olefinic protons) at $\tau$ 4.23, two-proton multiplet (protons on carbon bearing bromine) at *ca.* $\tau$ 5.3, and eight-proton multiplet (remaining protons) at *ca.* $\tau$ 7.2.

*Anal.* Calcd for $C_{10}H_{12}Br_4$: C, 26.58; H, 2.68; Br, 70.74. Found: C, 26.80; H, 2.68; Br, 71.10.

**2,3,6,7-Tetrabromo-9,10-oxidodecahydronaphthalene (15). a. From Oxide 10.** A solution of bromine (15 g, 0.094 mole) in chloroform (30 ml) was added dropwise during 30 min to a stirred solution of the oxide **10** (7 g, 0.047 mole) in chloroform (50 ml), the internal temperature being kept at 15–20° by ice cooling. The solution was allowed to stand at room temperature for 16 hr, and was then washed with sodium sulfite solution. The dried extract on evaporation to small volume and filtration yielded the tetrabromo oxide **15** in two crops (6.65 g, mp 161–163°, and 1.95 g, mp 161–162°; 39% yield). Crystallization from chloroform–petroleum ether (bp 40–60°) gave a pure sample: mp 163–164°; $\lambda_{max}^{KBr}$ 7.03, 7.56, 8.54, 9.20, 10.00, 10.13, and 10.52 $\mu$; nmr spectrum, four-proton multiplet (protons on carbon bearing bromine) at *ca.* $\tau$ 5.7, and eight-proton multiplet (aliphatic protons ) at *ca.* $\tau$ 6.8–7.9.

*Anal.* Calcd for $C_{10}H_{12}Br_4O$: C, 25.67; H, 2.59; Br, 68.32. Found: C, 25.48; H, 2.50; Br, 68.60.

Evaporation of the mother liquors yielded a yellow viscous oil (12.75 g, 58%), presumably consisting of a stereoisomeric mixture of **15**.

**b. From Tetrabromide 17.** A solution of the tetrabromide **17** (160 mg, 0.35 mmole) in chloroform (20 ml) was allowed to stand at room temperature for 2 weeks with a solution of perbenzoic acid in chloroform (containing 6.4 mg of active oxygen, 0.40 mmole). The product was isolated in the usual way, and chromatographed on alumina (30 g, Merck acid washed). Elution with pentane–ether (19:1) gave unchanged **17** (40 mg, 25%). Elution with pentane–ether (4:1) and crystallization from chloroform–petroleum ether (bp 40–60°) yielded the tetrabromo oxide **15** (18 mg, 11%), mp 161–163°, identified with the above-described compound by mixture melting point determination and infrared spectral comparison.

**1,6-Oxido[10]annulene (20) and 1-Benzoxepin (24) from Tetrabromo Oxide 15.** The crystalline tetrabromo oxide **15** (7.5 g, 0.016 mole) was added to a solution of potassium hydroxide (23 g, 0.41 mole) in ethanol (500 ml), and the mixture was stirred at 50–55° (internal temperature) for 20 min. A clear solution was obtained at first, followed by precipitation of potassium bromide. The mixture was cooled, and the potassium bromide (6.1 g, 0.051 mole) was removed by filtration. The filtrate was diluted with water, and the product was isolated by repeated ether extraction. The resulting material (2.1 g, yellow oil) consisted of a mixture of **20** and **24**, as evidenced by tlc, nmr, and infrared analysis. It was chromatographed on alumina (200 g, Alcoa F-20). Pentane–ether (49:1) eluted successively **24**, mixtures of **24** and **20** (separated by rechromatography on alumina), and **20**; ether eluted noncrystalline material (*ca.* 0.2 g, carbonyl infrared band), which was not further investigated.

1-Benzoxepin (**24**) (0.47 g, 20%) was obtained as a yellow liquid: bp 50° (bath temperature, 0.5 mm); $n^{26}D$ 1.6034; homogeneous by glpc analysis (SE-30 silicone, 120°); $\lambda_{max}^{film}$ 6.08, 6.26, 6.74, 6.92, 7.89, 8.05, 8.19, 8.40, 8.52, 9.07, 9.59, 10.59, 11.13, 12.04, 12.67, 12.97, 13.30, and 14.20 $\mu$; $\lambda_{max}^{EtOH}$ 211 m$\mu$ ($\epsilon$ 14,700), 231 (10,700), and 288 (2900); nmr spectrum, see Discussion.

*Anal.* Calcd for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.08; H, 5.64.

Substance **24** is rather unstable. A pentane solution on being allowed to stand without protection from daylight gradually decomposed, a white precipitate being deposited. The neat liquid under these conditions had almost completely decomposed after 2 weeks.

1,6-Oxido[10]annulene (**20**) (1.15 g, 50%) formed light yellow crystals from pentane; mp 52–53°, raised to mp 53–54° by sublimation at 60° (0.1 mm); $\lambda_{max}^{KBr}$ 6.51, 6.94, 7.53, 8.37, 8.69, 8.98, 10.21, 10.41, 11.58, 11.75, 12.46, 13.33, 13.42, and 14.46 $\mu$; $\lambda_{max}^{EtOH}$ 255 m$\mu$ ($\epsilon$ 74,000), 299 (6900), and complex band at *ca.* 393 (240) (see Figure 1); nmr spectrum, see Discussion and Figure 2. The substance had a characteristic smell, similar to naphthalene.

*Anal.* Calcd for $C_{10}H_8O$: C, 83.31; H, 5.59. Found: C, 83.05; H, 5.59.

Substance **20** is relatively stable; a pentane solution could be kept at room temperature without protection from daylight for several months without appreciable decomposition, while the solid under these conditions was almost unchanged after one month.

**Hydrogenation of 1-Benzoxepin (24) to 2,3,4,5-Tetrahydro-1-benzoxepin (25).** A solution of **24** (100 mg) in pentane (20 ml) was stirred in hydrogen over a 10% palladium–charcoal catalyst (*ca.* 50 mg), at room temperature and atmospheric pressure, until uptake ceased (*ca.* 30 min). The catalyst was removed and the solvent was evaporated. Distillation of the residue at 80° (bath temperature, 0.2 mm) and crystallization from pentane led to the tetrahydro derivative **25**, mp 27–29° (lit.[19] mp 28–29°). An authentic sample (mp 28–30°) was prepared by the method of Baddeley, *et al.*,[19] and identity was established by mixture melting point determination and infrared spectral comparison.

**Treatment of 1,6-Oxido[10]annulene (20) and 1-Benzoxepin (24) with Potassium Hydroxide.** A solution of **20** (40 mg) and potassium hydroxide (230 mg) in ethanol (50 ml) was heated at 50–55° (internal temperature) for 20 min. Addition of water and extraction with pentane led to unchanged starting material (39 mg), mp 51–52°.

Similarly **24,** (15 mg) was heated with potassium hydroxide (140 mg) in ethanol (30 ml) at 50–55° for 20 min. Unchanged starting material (14 mg) was then recovered.

**Rearrangement of 1,6-Oxido[10]annulene (20) by Chromatography. a. On Alkaline Alumina.** Chromatography of **20** (40 mg) on alkaline alumina (40 g, Alcoa F-20) in the usual way, or after allowing the substance to remain on the column for 16 hr before elution, caused no significant change.

**b. On Acid-Washed Alumina.** Chromatography of **20** (40 mg) on alumina (40 g, Merck acid washed) in the usual way resulted in no significant change. Allowing the substance to remain on the column for 16 hr before elution yielded successively 1-benzoxepin (**24**) (27 mg, 67%), unchanged **20** (10 mg, 25%), and $\alpha$-naphthol (1 mg, 2.5%). The products were identified with authentic samples by ultraviolet, infrared, and tlc comparison.

**c. On Silica Gel.** Chromatography of **20** (40 mg) on silica gel (40 g, Mallinckrodt) in the usual way again resulted in no significant change. Allowing the substance to remain on the column for 16 hr before elution gave successively 1-benzoxepin (**24**) (20 mg, 50%), unchanged **20** (16 mg, 40%), and $\alpha$-naphthol (1 mg, 2.5%).

Treatment of 1-benzoxepin (**24**) under all the conditions mentioned above under a, b, and c, resulted in no appreciable change.

**Rearrangement of 1,6-Oxido[10]annulene (20) with Boron Trifluoride.** Boron trifluoride etherate (five drops) was added dropwise to a solution of **20** (23 mg) in chloroform (7 ml). The resulting solution (an aliquot on dilution with hexane showed the typical ultraviolet spectrum of $\alpha$-naphthol) was poured into water. Isolation with ether and chromatography on silica gel (10 g, Mallinckrodt) gave 1-benzoxepin (**24**) (0.5 mg, 2%; determined spectroscopically), followed by $\alpha$-naphthol (16 mg, 70%), mp 95–96°. Both substances were identified by comparison with authentic samples. No trace of $\beta$-naphthol could be detected.

**Rearrangement of 1,6-Oxido[10]annulene (20) with Aqueous Acetic Acid.** A stirred suspension of **20** (60 mg) in acetic acid (3 ml) and water (27 ml) was heated at *ca.* 50° (internal temperature) for 2 hr. The product was then isolated with ether and chromatographed on silica gel (10 g, Mallinckrodt). Elution with pentane yielded 1-benzoxepin (**24**) (15 mg, 25%), identified by comparison with an authentic sample. Elution with pentane–ether (9:1) gave a *ca.* 1:1 mixture of α- and β-naphthol (30 mg, 50%). This mixture was separated by preparative tlc, and each component was identified by comparison with an authentic sample.

**Rearrangement of 1-Benzoxepin (24) with Acids. a. With Sulfuric Acid.** Concentrated sulfuric acid (5 ml) was added dropwise to a solution of **24** (70 mg) in ethanol (2 ml), with stirring and ice cooling. The green-red solution was immediately poured into water, and extracted with ether. Chromatography on alumina (10 g, Merck acid washed) then yielded unchanged 1-benzoxepin (1 mg, determined spectroscopically), followed by α-naphthol (6 mg, 9%), identified with an authentic sample. Subsequently, phenolic material (7 mg) was eluted, $\lambda_{max}^{EtOH}$ 282 mμ (shifted to $\lambda_{max}$ 328 mμ on addition of sodium hydroxide), which was not investigated further.

**b. With Boron Trifluoride.** Boron trifluoride etherate (six drops) was added to a solution of 1-benzoxepin (12 mg) in chloroform (3 ml). Addition of water, isolation with ether, and chromatography on silica gel (5 g, Mallinckrodt) yielded unchanged starting material (9 mg), followed by traces of α-naphthol (identified by the ultraviolet spectrum and tlc analysis).

**Hydrogenation of 1,6-Oxido[10]annulene (20). a. To Tetralin.** A solution of **20** (105 mg) in pentane (20 ml) was stirred in hydrogen over a 10% palladium–charcoal catalyst (*ca.* 50 mg) at room temperature and atmospheric pressure. About 1 molar equiv of hydrogen was absorbed in 5 min, and uptake then became slow. The reaction was terminated after 40 hr, when 3.2 molar equiv of hydrogen had been absorbed. Removal of the catalyst and solvent left a liquid residue (96 mg); this consisted of tetralin (*ca.* 95% purity), as evidenced by glpc analysis (SE-30 silicone, 120°) and comparison of the infrared, ultraviolet, and nmr spectra with those of an authentic sample.

**b. To Naphthalene.** Substance **29** (80 mg) was hydrogenated in ethanol (20 ml) over a 10% palladium–charcoal catalyst (*ca.* 50 mg) at room temperature and atmospheric pressure. The reaction was terminated after 5 min, when 1.05 molar equiv of hydrogen had been absorbed. Removal of the catalyst and solvent gave a crystalline residue (71 mg), which consisted of almost pure naphthalene as evidenced by comparison with an authentic sample.

**Lithium Aluminum Hydride Reduction of 1,6-Oxido[10]annulene (20) to Naphthalene.** A solution of **20** (50 mg) and lithium aluminum hydride (200 mg) in dry ether (40 ml) was boiled under reflux for 20 hr. The resulting solution (an aliquot on dilution with ether showed the typical ultraviolet spectrum of naphthalene) was then poured into water. The product was extracted with ether and chromatographed on alumina (10 g, Alcoa F-20). Elution with pentane gave naphthalene (33 mg, 74%), mp 78–79°, identified by comparison with an authentic sample. Subsequent elution with pentane–ether (15:1) yielded unchanged **20** (5 mg, 10%).

**Nitration of 1,6-Oxido[10]annulene (20).** Cupric nitrate trihydrate (1 g, 4.14 mmoles) was added to a solution of **20** (220 mg, 1.53 mmoles) in acetic anhydride (8 ml). The mixture was stirred at room temperature for 10 min, and was then poured into ice–water. Isolation with ether led to a yellow oil, which was chromatographed on alumina (30 g, Merck acid washed). Elution with pentane–ether (6:1) gave 2-nitro-1,6-oxido[10]annulene (**27**) (61 mg), mp 83–84°. Crystallization from ether–pentane yielded yellow-orange crystals: mp 86–87°; $\lambda_{max}^{KBr}$ 6.29, 6.47, 6.67, 7.53, 7.62, 8.48, 8.69, 8.88, 10.61, 11.40, 11.87, 12.07, 12.73, 13.19, and 13.48 μ; $\lambda_{max}^{EtOH}$ 238 mμ (ε 24,300), 283 (15,400), 365 (6700), and *ca.* 425 sh (1600); nmr spectrum, see Discussion. The substance was homogeneous by tlc.

*Anal.* Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73. Found: C, 63.07; H, 3.56.

Further elution with pentane–ether (6:1) gave a yellow oily mixture of **27** and **26** (130 mg, see below). Finally, pentane–ether (5:2) furnished material (13 mg), which may be a dinitro compound, but which was not investigated further.

The mixed nitro compounds **27** and **26** (130 mg) were rechromatographed on alumina (60 g, Merck acid washed). Elution with pentane–ether (6:1) yielded a further 25 mg of **27**, mp 83–85° (total yield, 86 mg, 30%). Further elution with this solvent mixture then gave a mixture of **27** and **26** (23 mg), followed by 3-nitro-1,6-oxido[10]annulene (**26**) (81 mg, 28%), mp 46–47°. Crystallization from ether–pentane furnished yellow crystals: mp 48–49°; $\lambda_{max}^{KBr}$ 6.28, 6.45, 6.71, 7.56, 8.05, 8.52, 8.89, 9.70, 10.21, 10.94, 11.45, 11.78, 12.19, 12.68, and 13.44 μ; $\lambda_{max}^{EtOH}$ 242 mμ (ε 21,500), 279 (26,500), 349 (7500), and *ca.* 425 sh (650); nmr spectrum, see Discussion. The substance was homogeneous by tlc.

*Anal.* Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.41. Found: C, 63.58; H, 3.98; N, 7.47.

**Acylation of 1,6-Oxido[10]annulene (20).** Boron trifluoride etherate (ten drops) was added dropwise to a solution of **20** (70 mg) and acetic anhydride (0.5 ml) in chloroform (15 ml). The resulting solution (an aliquot on dilution with hexane showed the typical ultraviolet spectrum of α-naphthyl acetate) was poured into sodium bicarbonate solution. Isolation with ether led to material which was chromatographed on alumina (30 g, Merck acid washed). The first substance eluted was α-naphthyl acetate (65 mg, 72%), mp 46–47°. This was followed by α-naphthol (6 mg, 9%), mp 95–96°, presumably formed by saponification of the acetate during chromatography. Both substances were identified by direct comparison with authentic samples.

**Treatment of 1,6-Oxido[10]annulene (20) with Maleic Anhydride.** A solution of **20** (30 mg, 0.2 mmole) and maleic anhydride (140 mg, 1.4 mmoles) in benzene (20 ml) was boiled under reflux for 2 hr. Chromatography then led to recovered **20** (29 mg, 97%), mp 51–52°.

**Bromination of 1,6-Oxido[10]annulene (20).** A solution of bromine (400 mg, 2.5 mmoles) in chloroform (15 ml) was added dropwise during 10 min to a stirred solution of **20** (60 mg, 0.4 mmole) in chloroform (10 ml) at 28°. The solution was stirred for a further 10 min, and was then poured into water. Chromatography of the product on alumina (30 g, Merck acid washed) and elution with pentane–ether (15:1) yielded two isomeric tetrabromides.

The tetrabromide eluted first (125 mg, 65%) on crystallization from petroleum ether (bp 40–60°) showed mp 156–158°; end absorption only in the ultraviolet spectrum; $\lambda_{max}^{KBr}$ 6.10, 7.18, 7.40, 8.28, 8.53, 8.71, 8.75, 9.71, 9.82, 10.65, 10.77, 11.41, 12.45, 12.55, 13.25, 14.01, and 14.45 μ; nmr spectrum, complex band at τ 4.1–4.9.

*Anal.* Calcd for $C_{10}H_8Br_4O$: C, 25.89; H, 1.74; Br, 68.92. Found: C, 26.18; H, 1.63; Br, 68.42.

The tetrabromide eluted later (20 mg, 10%) on crystallization from petroleum ether (bp 40–60°) exhibited mp 153–155°; end absorption only in the ultraviolet spectrum; $\lambda_{max}^{KBr}$ 7.18, 7.94, 8.73, 8.90, 10.78, 11.39, 12.04, 12.49, 12.91, and 13.78 μ.

*Anal.* Calcd for $C_{10}H_8Br_4O$: C, 25.89; H, 1.74. Found: C, 26.23; H, 1.81.

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