

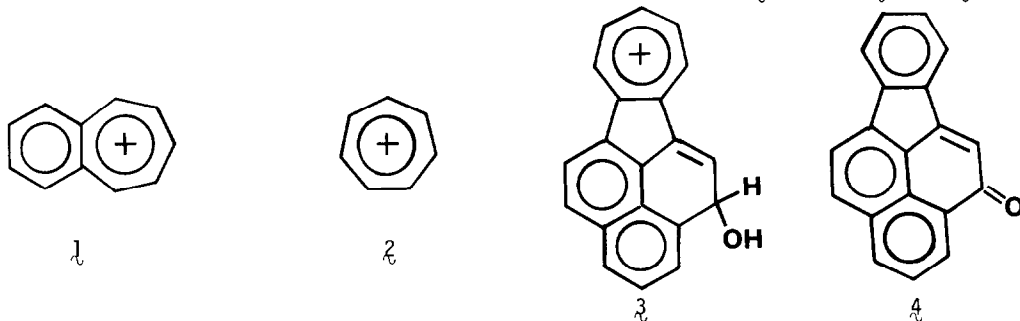
## THE OXIDATION OF THE BENZOTROPYLIUM CATION<sup>1</sup>

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**Abstract:** Oxidation of benzotropylium (1) fluoborate with Na<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>O<sub>2</sub> gives the benzotropones, 5 and 6, as the major products with no naphthalene (9) or other ring contracted products formed. Oxidation with m-chloroperoxybenzoic acid produces a small amount of naphthaldehydes (10 and 11) and even less naphthalene, along with the benzotropones, while oxidation with H<sub>2</sub>O<sub>2</sub> and t-butyl peroxyacetate gives slightly more of the ring contracted naphthaldehydes than benzotropones, in addition to a small quantity of naphthalene. All reactions produce some 1,2-benzotropilidene (8).

Prompted by several recent communications concerning the oxidation of tropylium cations,<sup>3-5</sup> and our continuing interest in the chemistry of benzotrotyl type free radicals and cationic species,<sup>6,7</sup> we examined the oxidation of the benzotropylium cation (1) with a variety of peroxidic reagents. We were particularly intrigued with the observations that the tropylium cation (2) (and a presumed, more highly annulated derivative, 3) could lose a carbon atom when reacted with various peroxidic substances, and give benzene from 2<sup>3,4</sup> (and 4 from 3).<sup>5</sup> Indeed,

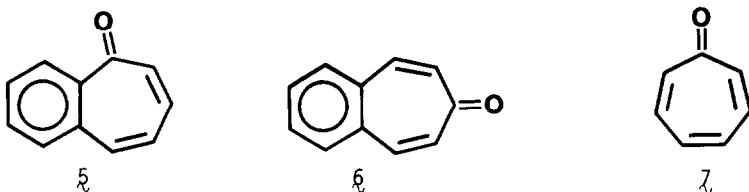


an earlier report<sup>8</sup> of the reaction of 2 with H<sub>2</sub>O<sub>2</sub> indicated that benzene was formed in over 82% yield. The more recent studies of Ando,<sup>3,4</sup> in which ion 2 was reacted with Na<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>O<sub>2</sub>, indicated that benzene, benzaldehyde and tropilidene were formed in equal amounts, in approximately 75% overall yield. In contrast to these results, other reported oxidations of 2 with non-peroxidic oxidizing agents such as chromic acid,<sup>9</sup> silver oxide,<sup>9</sup> and dilute permanganate<sup>10</sup> gave the ring contracted product, benzaldehyde, which has the same number of carbon atoms.

Our interest in these oxidations is the result of our having observed naphthalene

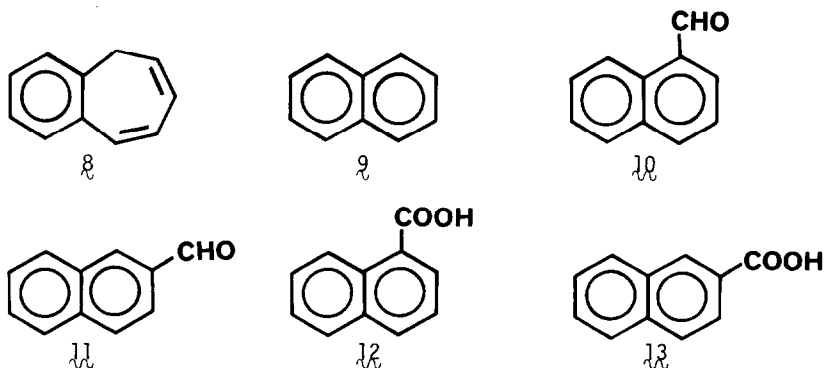
formation in free radical reactions of benzonorcaradienyl peroxide systems were we have shown that the free radicals produced, contain polar character.<sup>6</sup> It is possible, in these studies, that the naphthalene was derived from the benzotropylium ion ( $\lambda$ ) which could have been produced in those reactions.

We have thus examined the reactions of benzotropylium ( $\lambda$ ) fluoborate with a series of peroxidic reagents and, contrary to the results of the studies of the tropylium ion ( $\zeta$ ) itself, we find little, if any, naphthalene. Further, our results with  $\lambda$  are quite different from those of  $\zeta$  in that with all reagents studied major products are the benzotropones,  $\xi$  and  $\delta$ .<sup>11,12</sup> Tropone ( $\zeta$ ) has never been reported in any of the tropylium ion oxidations.



The table below shows the peroxidic reagent and solvent employed in the oxidations of benzotropylium ( $\lambda$ ) fluoborate. The mole ratio of  $\lambda$ :oxidant was 1:2. The absolute yield of products, determined by GLC or HPLC, is shown in the table, along with a "corrected" value of the absolute yield in parentheses. This "corrected" value, which more nearly estimates the true percentage yields obtained in the reactions, is provided because of further oxidation of some of the primary products.

The products of these oxidation reactions, in addition to  $\xi$ ,  $\delta$  and 1,2-benzotropolidene ( $\eta$ ), which were identified (by comparison with authentic samples) were naphthalene ( $\theta$ ),  $\alpha$ -naphthaldehyde ( $\lambda\theta$ ),  $\beta$ -naphthaldehyde ( $\lambda\lambda$ ),  $\alpha$ -naphthoic acid ( $\lambda\kappa$ ) and  $\beta$ -naphthoic acid ( $\lambda\lambda\kappa$ ).



The control experiments showed that 1,2-benzotropolidene ( $\eta$ ) was oxidized slowly to the benzotropones,  $\xi$  and  $\delta$ , with  $\text{Na}_2\text{O}_2$ ,  $\text{KO}_2$ ,  $\text{H}_2\text{O}_2$  and *t*-butyl peroxyacetate. In addition, the two naphthaldehydes,  $\lambda\theta$  and  $\lambda\lambda$ , were oxidized essentially completely to the corresponding naphthoic acids,  $\lambda\kappa$  and  $\lambda\lambda\kappa$ , with  $\text{H}_2\text{O}_2$  and *t*-butyl peroxyacetate under the reaction conditions.

The yield corrections are then made in the following way: the amount of benzotropilidene,  $\delta$ , (or other product) oxidized by itself (with the oxidant, under the same reaction conditions, and time allowed for reaction) was observed and then it was assumed that half this amount reacted during the course of the benzotropylium ion oxidation. The assumption is made that the benzotropilidene ( $\delta$ ; or other product) is produced at a steady rate during the reaction. Also, half of the benzotropones,  $\xi$  and  $\zeta$  (or other product), formed by reaction of the benzotropilidene,  $\delta$  (or other primary product), by itself, will be formed by this route from the benzotropylium ion ( $\lambda$ ). It can be seen that the corrections are fairly small, particularly since

Table - Oxidation of Benzotropylium Fluoroborate

| Reagent/solvent   | Products - absolute yield (corrected yield) <sup>a</sup> |        |          |         |           |        |       |          |
|---|--|--------|----------|---------|-----------|--------|-------|----------|
|   | $\delta$   | $\eta$ | $\xi$    | $\zeta$ | $\lambda$ | $\mu$  | $\nu$ | $\omega$ |
| Na <sub>2</sub> O <sub>2</sub> /Me <sub>2</sub> SO              | 4(5)   | --     | 4(4)     | 56(52)  | Tr        | Tr     | --    | --       |
| Na <sub>2</sub> O <sub>2</sub> /CH <sub>2</sub> Cl <sub>2</sub> | 15(16)   | --     | 14(14)   | 45(43)  | Tr        | Tr     | --    | --       |
| KO <sub>2</sub> /DMF  | 4(5)   | --     | 4(4)     | 25(23)  | Tr        | Tr     | --    | --       |
| 90% H <sub>2</sub> O <sub>2</sub> /THF                          | 0.5(0.6)   | 0.9    | 13(13)   | 3(3)    | 2(7)      | 3(16)  | 5(0)  | 13(0)    |
| 30% H <sub>2</sub> O <sub>2</sub> /THF                          | 1.2(1.3)   | 2      | 13(13)   | 9(9)    | 9(11)     | 13(17) | 2(0)  | 4(0)     |
| <i>m</i> -CPBA <sup>b</sup> /CH <sub>2</sub> Cl <sub>2</sub>    | 10(10)   | 0.7    | 5(5)     | 17(17)  | 3(3)      | Tr     | --    | --       |
| <i>t</i> -BPA <sup>c</sup> /CH <sub>2</sub> Cl <sub>2</sub>     | 0.4(0.4)   | 1.0    | 0.2(0.2) | 6(6)    | Tr(4)     | Tr(8)  | 4(0)  | 8(0)     |

a - see text for method of correction

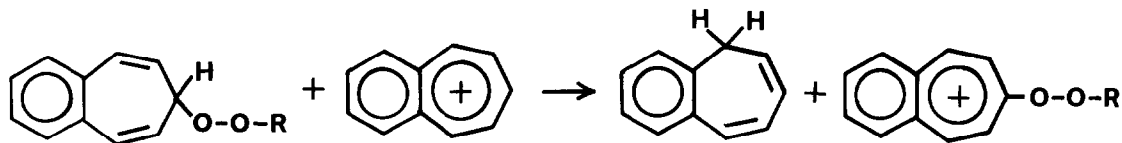
b - *m*-chloroperoxybenzoic acid

c - *t*-butyl peroxyacetate

only small amounts of the benzotropones ( $\xi$  and  $\zeta$ ) are formed from 1,2-benzotropilidene ( $\delta$ ) in the time allowed for reaction.

The following are the conclusions which can be drawn from the data presented. Very little naphthalene is formed in any of the reactions but where small amounts are formed, there is also formed 3-28% of ring contracted products, the naphthaldehydes ( $\lambda$  and  $\mu$ ). These three products ( $\eta$ - $\mu$ ), may well be linked mechanistically. In all cases the benzotropones ( $\xi$  and  $\zeta$ ) are major products and only in the case of H<sub>2</sub>O<sub>2</sub> and *t*-butyl peroxyacetate are they not the most abundant products.

The 1,2-benzotropilidene ( $\delta$ ), which is analogous to the tropilidene observed in the oxidation of  $\zeta$ , probably arises by a hydride transfer reaction<sup>3,4</sup> of the type shown below (R could



be one of several groups or even a negative charge). In addition, it is interesting to note that the ratio of  $\zeta$ : $\xi$  is considerably greater than unity in all cases except with H<sub>2</sub>O<sub>2</sub>, and, further, only with Na<sub>2</sub>O<sub>2</sub> and KO<sub>2</sub> are significant quantities of ring contracted products ( $\eta$ - $\mu$ )

not formed, while with the other oxidants they are.

The reasons for these observations and the mechanistic details of these reactions must await further study except to note that benzotropilidenes cannot readily form norcaradiene valence tautomers (because of loss of aromaticity) whereas tropilidenes can. This may explain why 7-membered ring products are formed from  $\lambda$  while ring contracted products are formed from  $\zeta$ .

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### References

- ( 1 ) This paper is dedicated to Professor William von Eggers Doering on the occasion of his 65th birthday.
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