Tetrahedron Letters No.49, pp. 4331-4334, 1970. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF 9,10-DIHYDRO-9,10-METHANOANTHRACEN-11-ONE (DIBENZONORBORNADIEN-11-ONE) AND NITRO SUBSTITUENT EFFECTS IN SOLVOLYSIS OF p-BROMOBENZENESULFONATES OF 9,10-DIHYDRO-9,10-METHANOANTHRACEN-11-OLS

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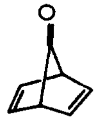
(Received in Japan 16 September 1970; received in UK for publication 22 September 1970)

Although long awaited in connection with the highly active research on norbornane and relevant ring systems, the syntheses of 7-norbornadienone (**1**) and its aromatic variants such as 9-benzonorbornadienone (**2**) and the titled ketone (**3**) are not yet available. We wish to report the first satisfactory synthesis of **3**[1-3] and the solvolytic behavior of p-bromobenzenesulfonates of 2-nitro-9,10-dihydro-9,10-methanoanthracen-11(syn and anti)-ols (**5**-OH and **6**-OH).[4]



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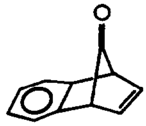

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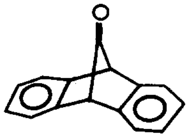

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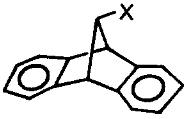

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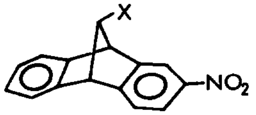

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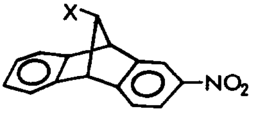

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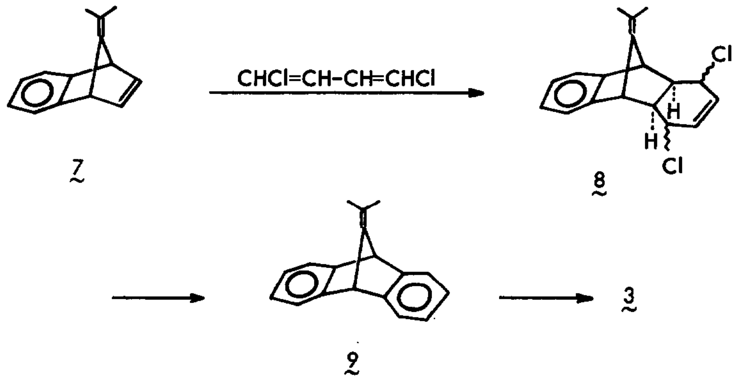
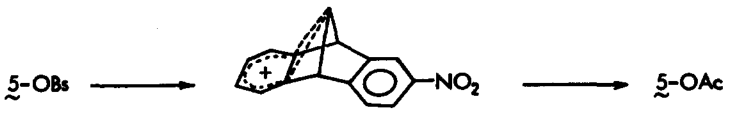
The Diels-Alder reaction of 7-isopropylidenebenzonorbornadiene (**7**)[5] with 1,4-dichlorobutadiene[6] in carbon tetrachloride (100° for 1 week) led to the adduct **8** melting at 123-129° and the butenobridge being indicated as exo by nmr,[7] which on treatment with potassium t-butoxide in dimethyl sulfoxide afforded the



dibenzo compound 9, dec 239-240°, in an overall yield of 28% from 7. The nmr peaks of eight aromatic protons centered at τ 2.91, of two bridgehead protons at τ 5.25 (singlet), and of six methyl protons at τ 8.42 (singlet) were entirely consistent with the present structure. Ozonolysis of 9 in methylene dichloride at -25° gave 3 (no sharp mp) in a stable form. Rapid and quantitative conversion of 3 into anthracene was observed in boiling benzene.

The alcohol 4-OH was obtained by reduction of 3 with lithium aluminum hydride and, after acetylation, nitrated with fuming nitric acid in acetic anhydride. Analysis of the nmr peaks in hexadeuteriobenzene due to the aromatic protons and the proton α to the acetoxyl group (triplet, at τ 5.00 for 5-OAc and 5.10 for 6-OAc) indicated production of a mixture of 5-OAc and 6-OAc in the ratio of 79 : 21, respectively.[8-9] After hydrolysis, 5-OH, mp 122-122.5°, and 6-OH, mp 132.5-133°, were isolated in pure states by preparative layer chromatography and converted into brosylates. Orientation of the hydroxyl groups in 5-OH and 6-OH was established by comparison of internal aryl π-hydrogen association in the infrared hydroxyl bands: for the parent 4-OH, an associated ν_{OH} at 3564 cm^{-1} only; for 5-OH, an associated ν_{OH} at 3573 cm^{-1} as well as a free ν_{OH} at 3624 cm^{-1} (therefore, $\Delta\nu$ = 51 cm^{-1}); for 6-OH, at 3561 as well as at 3624 cm^{-1} ($\Delta\nu$ = 63 cm^{-1}).

Solvolysis of the major brosylate, 5-OBs, in glacial acetic acid containing 1 vol% acetic anhydride and 1 equiv of sodium acetate was followed by titration of the p-bromobenzenesulfonic acid, formed, to obtain the rate constants; k_1 = (90.0°) 9.07×10^{-6} sec^{-1} and (120.0°) 2.09×10^{-4}. In contrast, the same reaction with the minor brosylate, 6-OBs, requires about 10 hr at 180° for completion. In spite of this



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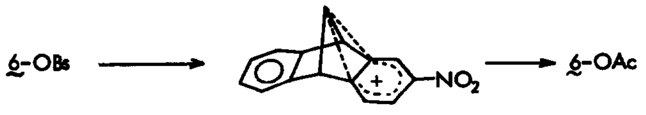

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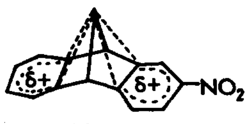

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large reactivity difference, the only detectable product by nmr was the acetate of complete retention of configuration from each of the brosylates.[10] The absence of any Wagner-Meerwein rearrangement and any solvent attack from the backside of the leaving group were demonstrated. Therefore, the solvolyses of **5**-OBs and **6**-OBs are discrete pathways, between which there is no crossover (no leakage). The formulation of the intermediate cations as such nonclassical structures as **10** and **11**, from **5**-OBs and **6**-OBs respectively, is consistent with the present results. However, charge distribution of a symmetrical type such as **12** is disproven. It is presumed that the energy barrier between the epimeric **10** and **11** is too great to permit a transformation from the less stable **11** into the more stable **10**, and instead, capture by solvent occures much more rapidly.

We are currently investigating whether or not an interconversion of the *anti* and *syn* epimeric cations is possible, by changing substituents on both the benzene rings, and thereby, the relative stabilities of both the cations.

REFERENCES

1. 9,10-Dihydro-9,10-methanoanthracen-11-ol (**4**-OH) was first synthesized by Meinwald and Miller[2] through a long reaction sequence starting from dibenzobicyclo[2.2.2]octadiene-2,3-dione. Oxidation of **4**-OH with chromium trioxide in pyridine at 4° was reported to yield crystals showing an intense absorption at 5.58 μ characteristic of a 7-keto[2.2.1] system. However, no account of the crystals was given besides the infrared band.

2. J. Meinwald and E. G. Miller, *Tetrahedron Letters*, 253 (1961).

3. On the general instability of **1** and its analogs due to ready decarbonylation, see (a) J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970), and, in particular, footnote 14 in this paper; (b) as a related review, M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, **65**,

261 (1965).

4. The terms *syn* and *anti* are defined as follows: substituents on the side of the nitrobenzene ring are *syn* and those on the other side are *anti*.

5. R. Muneyuki and H. Tanida, *J. Org. Chem.*, **31**, 1988 (1966).

6. Yu. A. Ol'dekop and R. V. Kaberdin, *Zhurnal Organicheskoi Khimii*, **1**, 873 (1965); *J. Org. Chem. USSR*, **1**, 876 (1965).

7. Satisfactory analyses were obtained for all new compounds described.

8. These ring systems show an unusually strong β-orientation in electrophilic aromatic substitution reactions. H. Tanida and R. Muneyuki, *J. Am. Chem. Soc.* **87**, 4794 (1965).

9. When an equivalent amount of nitric acid was used, 70% yield of the mononitro mixture was obtained with recovery of 16% **4**-OAc. Detectable amounts of dinitro compounds, with mononitration in both the benzene rings, were not obtained. This indicates that the presence of a nitro group in one benzene ring lowers the reactivity of the other benzene ring.

10. The two acetates show differing chemical shifts for the protons α to their AcO groups. This fact was used in the product studies.