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SYNTHESIS OF BICYCLO[4.2.0]OCTA-4,7-DIENE-2,3-DIONE

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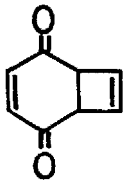
We have reported the synthesis of bicyclo[4.2.0]octa-3,7-diene-2,5-dione 1[1] which is the valence isomer of 2,4,7-cyclooctatriene-1,4-dione 2.[2] As to yet unknown 3,5,7-cyclooctatriene-1,2-dione 3, there can be two valence isomers, 4 and 5 (title compound) The isomer 4 may be in equilibrium with 3 at normal condition, whereas 5 may not be and hence should be an isolable compound. We here report the synthesis of 5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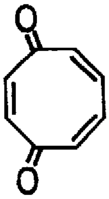
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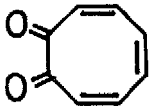
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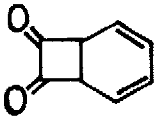
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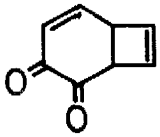
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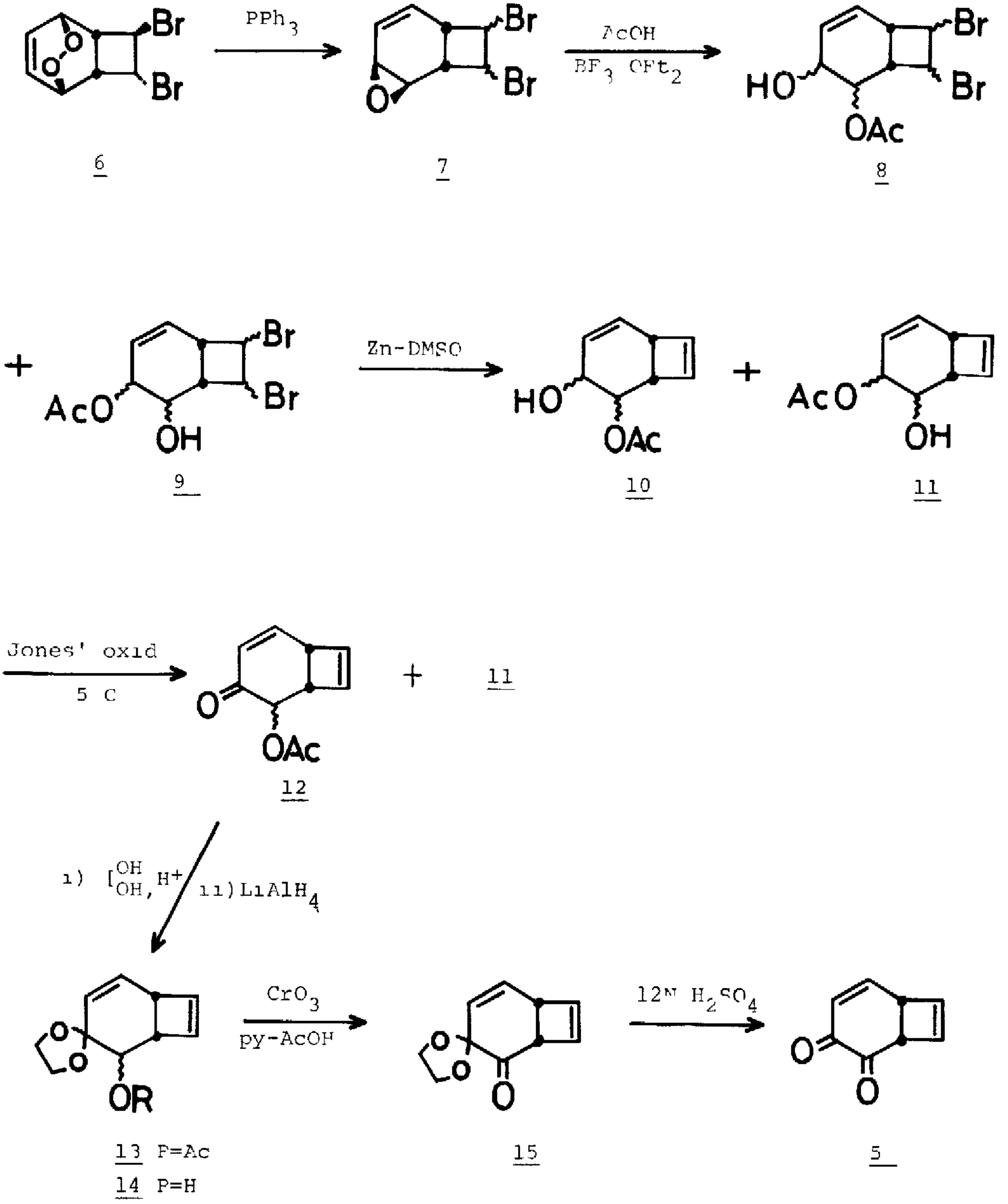
Treatment of *trans*-3,4-dibromo-9,10-dioxatricyclo[4.2 2 0^{2,5}]deca-7-ene 6[1] with triphenylphosphine (1 0 equiv) in benzene at 10-20°C afforded a crystalline mixture (mp 58-64°C) of two 1,2-epoxides, 7a (mp 82.5-83.5°C) and 7b (mp 38-39°C) (7a 7b = ca 5·3), in 71% yield. These are probably stereoisomers each other concerning to the stereochemical relationship of the epoxy group with the bromines. The configuration of the epoxy group may be *cis* to the methine protons, because the stereochemistry of the epidioxy group of 6 should be retained in this reaction. The separation of 7a and 7b was accomplished by repeated recrystallizations from n-hexane. The mixture was then converted into a mixture of the hydroxy-acetates, 8 and 9, by treatment with acetic acid in the presence of boron trifluoride etherate at room temperature in 88% yield. In view of the mechanism of acid catalized ring opening of epoxide, the relationship between the hydroxy and acetoxy group is probably *trans* , the hydroxy group being *cis* to the methine protons. Debromination of the mixture by heating with zinc dust in dimethyl sulfoxide at 70-90°C (exothermic reaction) for one hour gave a mixture of the debrominated hydroxy-acetates, 10 and 11 (ca 1 1 from PMR; bp 109-112°C/0.5 torr). Jones' oxidation of the mixture using 0.55 mol equivalent of chromium trioxide below 5°C preferably oxidized the allyl alcohol 10, giving an epimeric



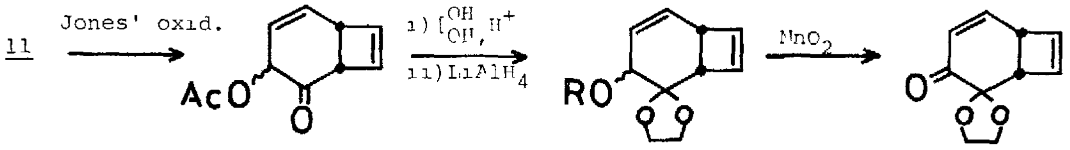
mixture of the enone-acetate 12 and almost pure unreacted 11 (mp 64-65°C), which were easily separated by silica gel chromatography, in 42% and 27% yield, respectively

Ketalization of 12 (ethylene glycol, p-TsOH, benzene reflux, 61%, mp of the major epimer, 108-109°C) and subsequent reduction with lithium aluminum hydride in tetrahydrofurane (quantitative) afforded the hydroxy-ketal 14 Oxidation of

14 with chromium trioxide in pyridine-acetic acid (3:2 in volume)[3] at room temperature for four hours afforded the keto-ketal 15 (mp 27-28°C) in 48% yield

When a benzene solution of 15 was vigorously stirred with 12N sulfuric acid for one hour, the desired diketone 3 came into the acid solution Successive extraction of the diluted aicd solution with methylene chloride gave 5 as yellow crystals of mp 56-57°C in 81% yield When a crude 15 was used, 5 was slightly contaminated with 1 which may be derived from a 1,4-hydroxy-acetate which was probably present as a slight impurity in the mixture of 8 and 9.

The recovered hydroxy-acetate 11 was also converted into the corresponding keto-ketal 19 (mp 66-67°C) by Jones' oxidation (room temperature), ketalization, reduction, and then oxidation with active manganese dioxide in 34% overall yield. The compound 19, however, more resists to acid hydrolysis and with 18N sulfuric acid it gave 5 in poor yield accompanied by appreciable decomposition of the material



16

17 R=Ac

18 R=H

19

In contrast to considerable thermal stability of 1[1], the α-diketone 5 is thermally less stable and undergoes a rearrangement at ca 160°C [4] Although 5 is moderately stable in acid solutions as used for the preparation, it is unstable to silica gel (Merck Kiesegel 60) and mostly decomposes in the column giving highly polar yet unidentified materials

The IR spectrum (KBr) of 5 shows carbonyl absorptions at 1710 and 1665 cm^{-1}, and double bonds at 1605 and 1550 cm^{-1} The electronic absorption maxima in ethanol are seen at 233 (ε 5300) and 328 nm (ε 1400) The mass spectrum shows the molecular ion and significant fragments at m/e 134 (M^+, 8%), 106 (M-CO, 21%), 78 (M-2CO, 75%), and 43 (100%). The PMR spectra in $CDCl_3$ and C_6D_6 are shown in the Figure, which support the assigned structure and in addition show a significant solvent effect.

In CF_3COOD, 5 slowly decomposed and completely disappeared in the PMR spectrum after two days at room temperature. During this time, no observable hydrogen exchanges with deuterium at the ring junctures of 5 were found as judged from the integrated area of the signals Accordingly, 5 is not equilibrated with the mono-enolized and the bis-enolized form (an antiaromatic benzocyclobutadiene) at the acidity of trifluoroacetic acid (pKa = 0 23), though the decomposition through enolization remains possible.

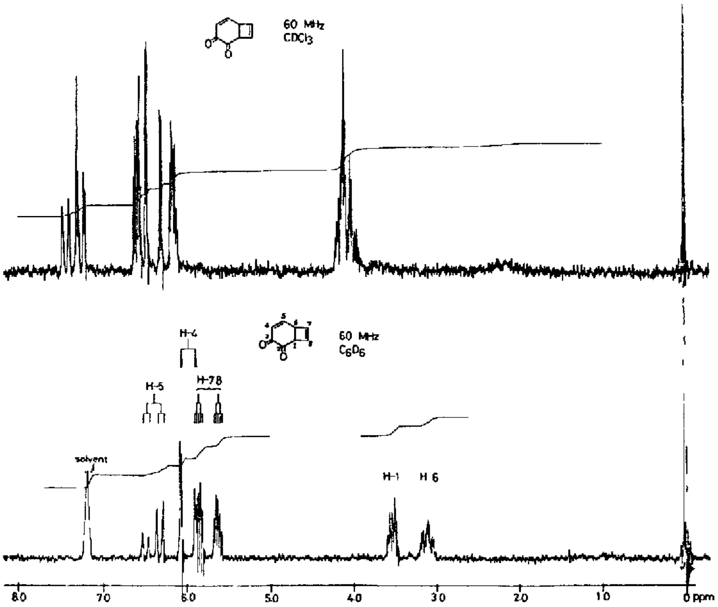


Figure. PMR Spectra of 5 in $CDCl_3$ (upper) and C_6D_6 (lower).

7a . PMR ($CDCl_3$, 100 MHz) δ = 3.15-3 45 (m, 4H), 4.26 (t, J = 8.0 Hz, 1H), 4 57 (t, 8.0, 1H), 5.80 (structured d, 10.0, 1H), 6.14 ppm (ddd, 10.0, 4.0, 1.8, 1H)

7b PMR ($CDCl_3$, 100 MHz) δ = 2.94 (dddd, 9.5, 6.8, 3.7, 0.8, 1H), 3.30 (m, 1H), 3.51 (br. t, 9 5, 1H), 3.58 (dd, 3.7, 0 8, 1H), 4.20 (dt, 6.8, 1.0, 1H), 4 68 (ddd, 9.5, 6.8, 0.5, 1H), 6.07 ppm (m, 2H)

15 : IR (KBr) ν = 1715, 1615, 1555 cm^{-1}, PMR ($CDCl_3$, 60 MHz) δ = 3.8-4.3 (m, 6H), 5.73 (dd, 10 0, 3.0, 1H), 6.18-6.40 ppm (m, 3H)

19 . IR (KBr) . ν = 1665, 1620, 1560 cm^{-1} UV (ethanol) λ = 223 (ε 5070), 344 nm (ε 78); PMR (CCl_4, 60 MHz) δ =3 3-4.3 (m, 6H), 5 87 (dd, 10.5, 1.0, 1H), 6.12 (dd, 2.5, 1.0, 1H), 6.35 (dt, 2.5, 1.0, 1H), 6.92 ppm (dd, 10.5, 4.5, 1H)

References and Notes

1) M. Oda, Y. Kayama, and Y. Kitahara, Tetrahedron Lett., 2019 (1974).
2) M. Oda, Y. Kayama, H. Miyazaki, and Y. Kitahara, Angew. Chem., 89, 414(1975); internat. edit., 14, 418 (1975).
3) This oxidizing condition gave 15 in better yield than the other methods we tried such as CrO_3-py_2[4] in pyridine, CrO_3-py_2 in CH_2Cl_2[5], and pyridinium chlorochromate.[6] Apparent superiority of this solvent system over pyridine only is higher solubility of the oxidant, and hence lesser amount of solvent is required (Addition of 1.5 g of CrO_3 into 10 ml of py-AcOH (3·2) gives a red-orange solution). Moreover the rate of oxidation seems faster, though yet qualitative, than in pyridine only.
4) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, J. Amer. Chem. Soc., 75, 422 (1953).
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7) The thermal rearrangement of 5 will be reported soon.