Pergamon

Tetrahedron Letters, Vol. 37, No. 49, pp. 8845-8848, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)02146-6

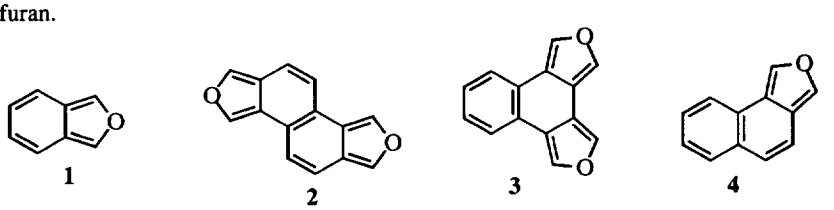
Naphtho[1,2-c;5,6-c]difuran, a Stable Isobenzofuran Derivative

Daniel W. Yu, Kathryn E. Preuss, Paulette R. Cassis, T. Dontem Dejikhangsar and Peter W. Dibble*

Department of Chemistry, University of Lethbridge, Lethbridge, Alberta, Canada, T1K 3M4

Abstract: The title compound, an interesting analog of isobenzofuran, was prepared in nine steps from 2,6-dimethylnaphthalene in an overall yield of 12%.

Isobenzofuran (**1**) and its derivatives continue to be materials of substantial interest for their electronic structure and their utility in the preparation of a wide variety of materials.[1-4] Many difurans have also been investigated as monomers useful in the preparation of Diels-Alder ladder polymers.[5-9] We wish to report the isolation of naphtho[1,2-c;5,6-c]difuran, **2**, an intriguing molecule that consists of two isobenzofuran moieties sharing a common face. Difuran **2** was be expected to be very different than its known isomer **3**,[5,9] which contains a fully aromatic benzene ring. The thermodynamic driving force for addition to the furan ring of **3** is small in comparison to **2**, in which 1,3-addition *forms* an aromatic benzenoid ring. On this basis, one might expect **2** to have reactivity more like that of isobenzofuran.



1 **2** **3** **4**

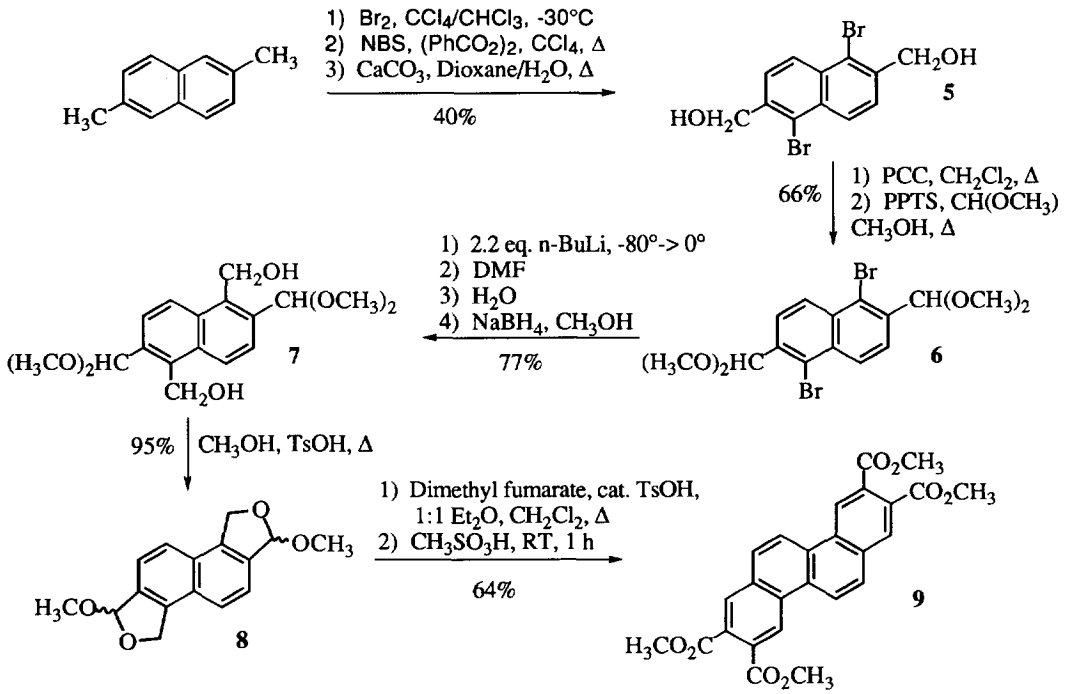
Figure 1: Isobenzofuran, naphtho[1,2-c;5,6-c]difuran, naphtho[1,2-c;3,4-c]difuran and naphtho[1,2-c]furan

We sought to prepare **2** via bis(acetal) **8** (Scheme 1) using methodology analogous to that used in the preparation of the acetal precursor to **4**,[10] is shown in Scheme 1. Electrophilic and subsequent radical bromination of 2,6-dimethylnaphthalene followed by hydrolysis gave dibromodiol **5**. Attempts to exchange the bromine atoms for an aldehyde functional group by treatment with 4 equivalents of n-BuLi followed by DMF were frustrated by the poor solubility of the starting material. Oxidation to a dialdehyde and acetalation gave **6** which proved to be a more viable substrate. The dianion formed by treatment of **6** with two equivalents of n-BuLi formed smoothly and was reacted with excess DMF. Reduction of the resulting dialdehyde with $NaBH_4$ gave diol **7** which was then cyclized to bisacetal **8** in methanol.

Acetals such as **8** are known to form benzo[c]furans under acid catalyzed conditions in which the furan is trapped *in situ* by a dienophile.[11] Treatment of **8** in diethyl ether/methylene chloride in the

presence of TsOH and excess dimethyl fumarate gave a complex mixture of diastereomeric adducts whose proton NMR was consistent with fumarate adducts of **2**. The Diels-Alder reaction can proceed via **2** itself, the monoelimination product **10** (Scheme 2) or both. The intermediacy of **2** in this reaction can be inferred by the observation of its spot in the thin layer chromatogram. The mixture of fumarate adducts was dissolved briefly in methanesulphonic acid to give a single substituted chrysene (**9**) via dehydration of the intermediate oxabicycloadducts. We have found methanesulphonic acid to be very effective (for oils) in these aromatization reactions[12] in comparison to other techniques, such as concentrated HCl.[10]

Scheme 1



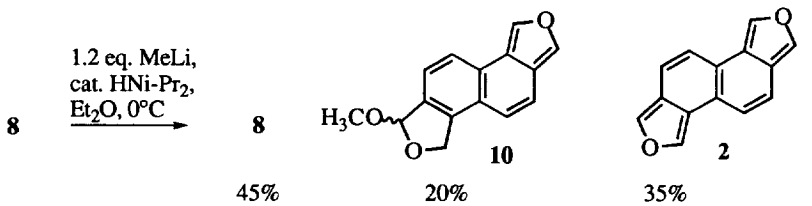
Isobenzofuran and related compounds can be isolated from acetal precursors by treatment with LDA (generated *in situ*)[13] Bis(acetal) **8**, when treated with 1 equivalent of LDA gave a mixture of starting material, mono-elimination product **10** and difuran **2** indicating the the elimination is not selective. Addition of excess LDA gave **2** in 64% yield.

The proton NMR shows doublets for the furan protons with a coupling constant of 1.6 Hz. The CH protons of the carbocyclic ring appear as an AB quartet (very nearly shift equivalent) and exhibit a

coupling constant of 9.3 Hz. These values are very close to those of the comparable protons in naphtho[1,2-c]furan, **4**.[14] The vicinal coupling constant of the carbocyclic protons (9.16 Hz in **1**)[15] suggests that **2** has a substantial polyene character and that, like isobenzofuran, it has substantial bond localization. The high resolution mass spectrum gives the molecular ion as the base peak. The fragmentation pattern consists of the loss of CO and subsequent loss of H, characteristic of benzo[c]furan derivatives.[16]

Somewhat to our surprise, **2** appears to be substantially more robust than isobenzofuran. The compound can be chromatographed on alumina and isolated as a solid at room temperature, whereas isobenzofuran polymerizes.[17] NMR samples of **2** in $CDCl_3$ show gradual decomposition over a day at room temperature. The gradual appearance of two aldehyde peaks in the proton spectrum indicates that hydrolysis of a furan ring is occuring rather than polymerization.

Scheme 2



Acknowledgements: We wish to thank the University of Lethbridge Research Fund and the Natural Sciences and Engineering Research Council for funding.

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(12) In 40 mL of 1:1 methylene chloride/diethyl ether was dissolved 100 mg **8** (0.37 mmol) and 112 mg dimethyl fumarate (0.78 mmol). A few crystals of p-toluenesulphonic acid (TsOH) were added and the mixture refluxed for 4 h. The solvent was removed under reduced pressure and the residue dissolved in 5 mL of methanesulphonic acid. After stirring for 1 hour, water was added and the mixture extracted with chloroform. The organic phase was separated, dried over $MgSO_4$, filtered and the solvent removed. The residue was recrystallized from methanol to give 109 mg (64%) of 2,3,8,9-Chrysenetetracarboxylic acid, tetramethyl ester, **9**; m.p. 265-266°C; RF 0.38 (5% MeOH in CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$) δ 4.02 (s, 6H), 4.04 (s, 6H), 8.14 (d, J=9 Hz, 2H), 8.41 (s, 2H), 8.88 (d, J=9 Hz, 2H), 9.18 (s, 2H); IR (KBr) 1723 (C=O), 1298, 1273, 1222, 1133 cm^{-1}; Analysis calc'd for $C_{26}H_{20}O_8$: C, 67.87; H, 4.38; found: C, 68.07; H, 4.06.

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(*Received in USA* 30 *September* 1996; *revised* 28 *October* 1996; *accepted* 1 *November* 1996)