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A Facile Rearrangement of a Bisalkynylbenzil via a Benzo[c]pyrylium Cation

Gerald Dyker*, Wolfgang Stirner, Gerald Henkel and Martin Köckerling

Institut für Synthesechemie, Fachbereich 6,
Gerhard-Mercator-Universität-GH Duisburg, Lotharstraße 1, D-47048 Duisburg, Germany

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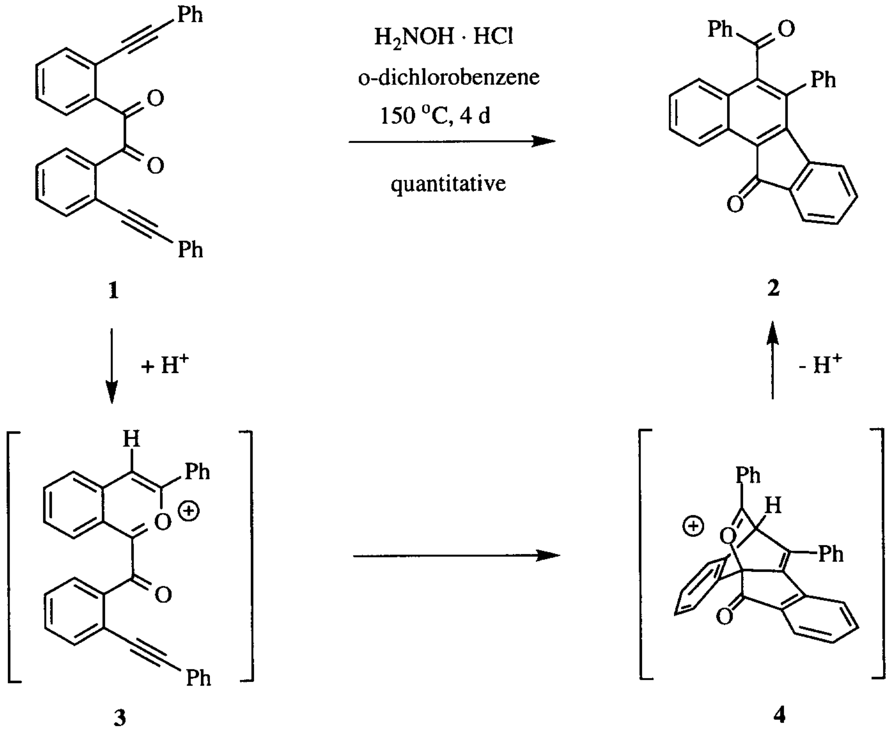
Abstract: Benzil **1** rearranges under acid catalysis by a domino process involving formation of a pyrylium cation, intramolecular Diels-Alder reaction and ring fragmentation. © 1999 Elsevier Science Ltd. All rights reserved.

In the course of our investigation of synthetic routes to biisoquinoline-bis-N-oxides[1] we anticipated, that the bisoxime of the benzil **1**[2] should cyclize to the target structure in analogy to the established method by Sakamoto et al..[3] Surprisingly, we could not find any evidence for oxime formation from **1** and hydroxylamine hydrochloride under various reaction conditions. Instead, after 10 h at 70 °C in ethanol a 13 % yield of the rearrangement product **2** was obtained, and under optimized conditions (o-dichlorobenzene, 140 °C, 4 d) the yield of **2** became quantitative according to the ^{1}H NMR of the crude product.[4] From the mass spectra it is clear that starting material **1** and product **2** have the same molecular mass. The IR spectrum of **2** shows the absorption of two distinguished carbonyl functions at 1696 and 1665 cm^{-1}. An X-ray structure analysis con-



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firmed the structure of the benzo[a]fluorenone **2** (Fig. 1).[5] For the ^{1}H NMR spectrum the multiplet of 1-H at 9.18 ppm (downfield shift by the neighbouring carbonyl group) and the signal of H-8 at 6.08 ppm are characteristic. The significant upfield shift of the latter signal is caused by the anisotropic effect of the phenyl group at C-7 fixed in an orthogonal conformation. The hindered rotation of this phenyl group is further responsible for the broadened signals in the ^{1}H NMR spectrum and for the total number of 28 different carbon atoms counted in the ^{13}C NMR spectrum.

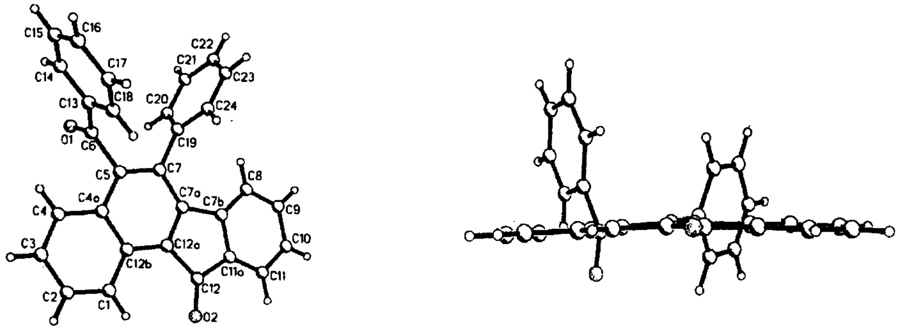

Figure 1: Views of the molecular structure of **2** in the crystal.

For the mechanistic interpretation of this rearrangement reaction we assume the formation of an aromatic benzopyrylium cation **3** after protonation of one of the equivalent alkyne functions. This type of reaction has some precedent in the similar formation of isoquinoline-N-oxides from oximes mentioned above.[3] An intramolecular Diels-Alder reaction[6] followed by a ring fragmentation of intermediate **4** is a straightforward route to the observed product **2**.

Currently we are investigating scope and limitations of domino processes initiated by the formation of benzopyrylium cations from functionalized alkynes.

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References and Notes

1. W. Stirner, Dissertation, Uni-GH Duisburg **1999**.
2. The bisalkyne **1** is synthesized from 2,2'-dibromobenzil (A. Terfort, H. Brunner, *J. Chem. Soc., Perkin. Trans. I* **1996**, 1467-1479.) by a twofold Sonogashira coupling reaction with phenyl acetylene.
3. T. Sakamoto, Y. Kondo, N. Miura, K. Hayashi, H. Yamanaka, *Heterocycles* **1986**, *24*, 2311-2314.
4. Selected spectroscopic and analytical data of **2**: orange crystals with mp 260-262 °C; ^{13}C NMR (CDCl$_3$): δ = 123.24 (d), 123.78 (d), 124.68 (d), 125.97 (d), 127.60 (s), 127.61 (d), 128.10 (d, br), 128.35 (d), 128.53 (d, 2C), 128.86 (d, br), 129.02 (d), 129.30 (d, br), 129.46 (s), 129.49 (d, 2C), 129.56 (d), 130.64 (d, br), 131.22 (s), 132.75 (s), 133.75 (d), 134.19 (d), 134.71 (s), 136.11 (s), 137.60 (s), 143.42 (s), 143.85 (s), 144.57 (s), 195.12 (s), 198.18 (s); Calc. C 87.78, H 4.42; found C 87.80, H 4.39.
5. X-ray data of compound **2** have been deposited at the Cambridge Crystallographic Data Centre (deposition number CCDC-133228). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax. (internat.)+ 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].
6. For Diels-Alder reactions of benzo[c]pyrylium salts, see: E. Kuznetsov, I. V. Shcherbakova, A. T. Balaban, *Adv. Heterocycl. Chem.* **1990**, *50*, 157-254, especially 219-220.