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σ-Bishomoaromatic Heterocycles: Reactivity and Synthesis of 3-Oxatetracyclo[3.3.0.0^{2,8}0^{4,6}]octane by Photolysis at 185 nm

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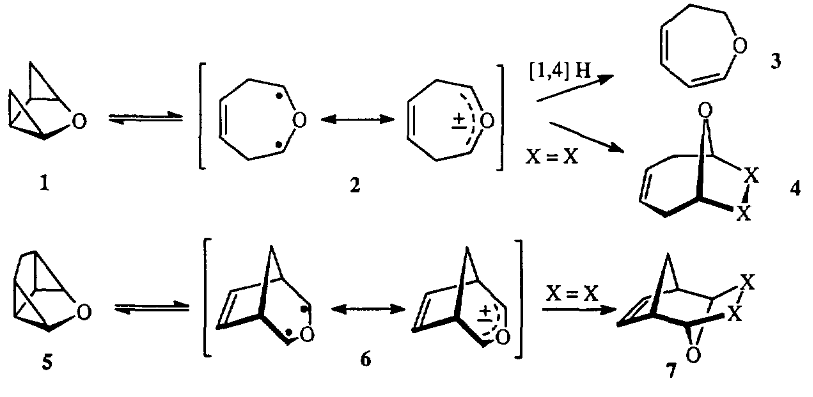
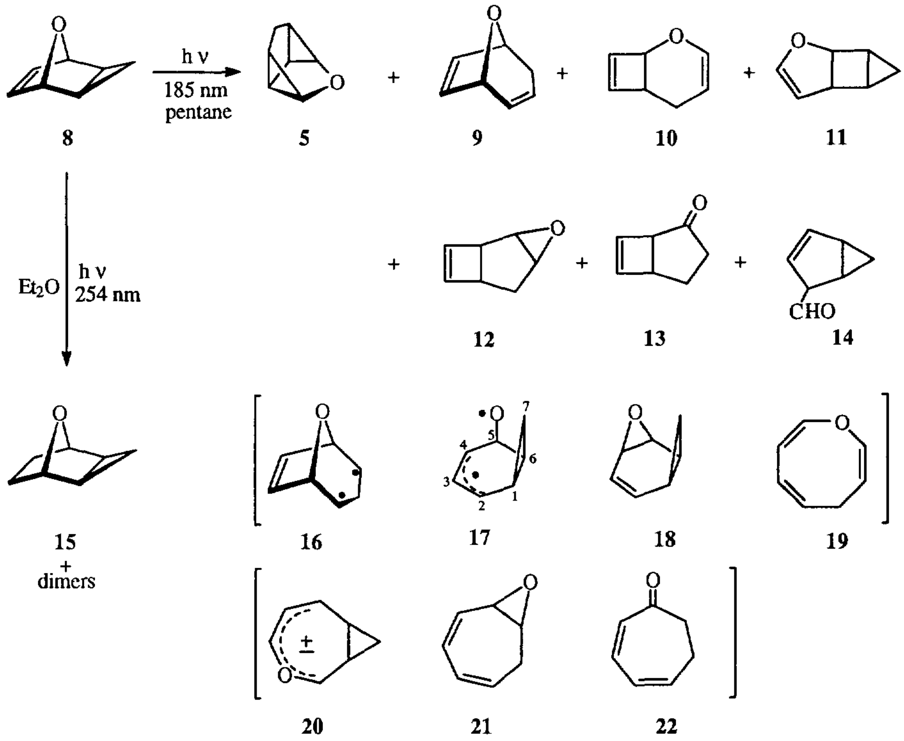
Abstract: The title compound 5 was produced by 185 nm photolysis of 8. The products of the 185 nm photolysis can be rationalized by the assumption of the two diradical intermediates 16 and 17. At a temperature between 150 and 200 °C 5 reacts with fumaronitrile 23 to give the adducts 7 and 26 in a ratio of about (5 : 1). The kinetic analysis of this reaction shows, that the adduct 7 is formed by 1,3 dipolar cycloaddition of intermediate carbonyl ylide 6.

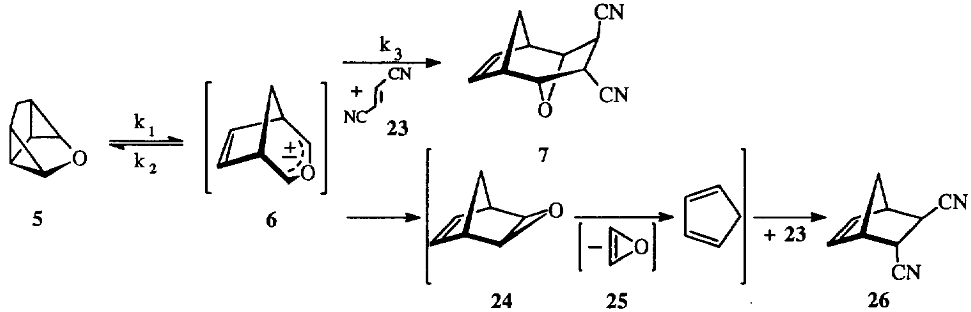
Carbonyl ylides - formally the products of an oxirane ring opening - have attracted great interest[1] (e.g. as reaction partners in 1,3-dipolar cycloadditions). Recently, it has been shown[2] that the thermolysis of *syn*-bishomofuran **1** offers an independent route to carbonyl ylide **2** which reacts either with π-acceptor substituted alkenes or alkynes (X=X) in the fashion of a 1,3-dipolar cycloaddition leading to cycloadducts of type **4** or rearranges in the absence of dipolarophiles to 2,3-dihydro-oxepine **3** involving an orbital-symmetry allowed sigmatropic [1,4]hydrogen shift. 7-Oxaquadricyclane[3], which can be regarded as bridged *syn*-bishomofuran derivative, shows similar reactive properties. Ring opening leads to the corresponding bicyclic carbonyl ylide which again either adds dipolarophiles to form cycloadducts or isomerizes to oxepine ⇌ benzene oxide. Both carbonyl ylides, described here, have channels of monomolecular orbital symmetry allowed reactions which prevents an extensive study of its reactivity.The methylene bridged *syn*-bishomofuran **5** does not have such a possibility and, therefore, should be a superior model. So far only two derivatives[4,5] of **5** are known which are thermally stable up to a temperature of 200 °C and 250 °C, respectively. Trapping experiments during their thermolyses do not provide any evidence of carbonyl ylide to be formed as a reactive intermediate. Electronic and steric effects may be responsible for the different behaviour of the substituted derivatives of **5** compared to that of parent **1** or 7-oxaquadricyclane. The purpose of this paper has been the synthesis of the parent methylene bridged *syn*-bishomofuran **5** and the study of its reactive behaviour.



Analogously to the successful photolysis of diester-substituted derivative of **8**[4] and the parent carbocyclic hydrocarbon **8** (with CH_2 instead of O)[7] the Diels-Alder adduct **8**[6] obtained from the reaction of furan with cyclopropene was photolyzed at 254 nm to result the product of hydrogenation **15** besides not isolated dimers. The photolysis of **8** at 185 nm in degassed and alkene-free pentane solution (Suprasil A quartz (Heräus), Hg-low-pressure lamp: HNS 20/10 U OZ (Osram) at 0 °C) led to a mixture of seven products in a ratio of 33 : 11 : 19 : 7 : 7 : 4 : 8 determined by GC (silicon oil OV 17, 25 m fused silica capillary, $p(H_2) = 17$psi, splitting: 1 : 80; corresponding to the compounds **5**[8], **9**, **10**, **11**[9], **12**[10], **13**[11], **14**[12]) which could partially separated by preparative GC (2 m ¼-inch column packed with 20 % silicon oil DC 550 on Chromosorb P 100 °C, carrier gas: He). The structures of the isolated products could be assigned by their NMR spectra or by comparison with authentic samples. The main product isolated in a purity > 95 % turned out to be the desired methylene bridged *syn*-bishomofuran **5**.



The results of the photolysis of **8** at 254 nm and 185 nm can be explained by the excitation of different chromophores. At 254 nm only the C=C double bond is excited leading to the saturated compound **15** by hydrogen abstraction from the solvent (diethyl ether) whereas at 185 nm the cyclopropane ring is additionally excited[13]. The observed products of the 185 nm photolysis can be rationalized by the assumption of the 1,3 diradical **16** to be one intermediate. Intramolecular addition of the radical centers to the double bond in **16** affords **5** and [1,2] hydrogen shift in **16** the oxabicyclooctadiene **9**. Cleavage of one C-O bond in **8** leads to diradical **17**, and a subsequent formation of a new C-O bond to *syn*-oxabishomobenzene **18**. The isomerization of **8** to **18** can be also the result of a photochemically induced sigmatropic [1,3]-O-shift. Compound **18** apparently undergoes already at 0 °C valence bond isomerization producing 4H-oxacin **19**[14] which is photochemically unstable to react further by electrocyclic ring-closure reaction leading to **10** and **11**. The minor products **12**, **13**, **14** can be derived from diradical intermediate **17**. Cleavage of bond C^1-C^6 followed by C-O bond formation or [1,2]-H-shift leads to **21** or **22**, which undergo photochemically induced electrocyclic ring-closures affording **12** and **13**, respectively. Cleavage of bond C^5-C^6 in **17** and subsequent formation of a bond between C^4 and C^6 produces **14**. The proposed mechanism of formation of **10**, **11** and **12** is supported by photolysis of the independently synthesized compounds **19**[9] and **21**[15]. The formation of **10** and **11** can be rationalized by a photochemically induced 1,3-diene → cyclobutene electrocyclization or by a 1,7-electrocyclic ring-closure in **19** leading to 3-oxabicyclo[5.1.0]heptadienyl ylide **20** followed by a well precedented 1,4 electrocyclization[9]. The photolysis of **19** at 185 nm produced **10** and **11** in the same ratio as that observed in the photolysis of **8**. Whereas the photolysis of **19** at 254 nm gave neither **10** nor **11**.



The methylene bridged *syn*-bishomofuran **5** is thermally much more stable than the parent *syn*-bishomofuran **1**. A thermolysis of **5** at 300 °C in the gas phase affords cyclohexa-1,4-diene-1-carbaldehyde and benzaldehyde in ratio of (1 : 3.5). In the presence of fumaronitrile **23** the *syn*-bishomofuran **5** already reacts at temperatures of about 150 to 200 °C to give adduct **7** as a major product and **26**[16] as a minor product (product ratio of about (5 : 1)). The structure of the new compound **7** could be assigned by its NMR spectra in which the vicinal coupling constants are in particular informative for the stereochemical assignment[8)]. The minor product turned out to be the adduct **26** resulting from Diels-Alder reaction of 1,3-cyclopentadiene with fumaronitrile. From the kinetic analysis of the disappearance of **5** and the appearance of **7** in dependence of the concentration of fumaronitrile **23** under pseudo-first-order conditions one can conclude that an intermediate, highly likely the carbonyl ylide **6**, reacts with fumaronitrile in the fashion of 1,3-dipolar cycloaddition and not the starting material **5**. This kinetic analysis allows us to calculate the rate constant of ring-opening **5** → **6** and the ratio of the rate constants of ring-closure and 1,3-dipolar cycloaddition in the transient intermediate **6** to be $k_1 = (1.61 \pm 0.13) \times 10^{-4} s^{-1}$ and $k_2/k_3 = (4.92 \pm 0.52)$ M at 179.6 °C. This result is in good agreement with that obtained for the parent *syn*-bishomofuran **1**[2]. In order to explain the formation of the minor product **26** we assume that the carbonyl ylide **6** can also undergo a disrotatory orbital-symmetry forbidden electrocyclic ring closure leading to the norbornadieneoxide **24** followed by *retro*-Diels-Alder reaction producing 1,3-cyclopentadiene, which in turn reacts with an excess of fumaronitrile **23** to give the observed adduct **26**, and not detectable oxirene **25**. With this explanation the question remains open: why we did not observe cyclopentadiene in the gas-phase thermolysis of **5**. A reasonable answer could be that the norbornadieneoxide **24**, which may be also an intermediate in the formation of the gas-phase products, is known to rearrange in the presence of traces of acid affording *endo*-bicyclo[3.1.0]hex-2-ene-7-carbaldehyde[17] which reacts further to the observed products (cyclohexa-1,4-diene-1-carbaldehyde and benzaldehyde). The observation of product **26** indicates that norbonadieneoxide **24** may be a precursor of the hitherto unknown oxirene **25** which may be characterized under acid-free conditions in a flash pyrolysis. Investigations of this reaction are in progress.

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References and Notes

1. Review: Huisgsen, R., *Angew. Chem.* **1977**, *89*, 689; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 572; Turro, N. J.; Cha, Y. *Tetrahedron Lett.* **1987**, *28*, 1723.
2. Golz, T.; Hammes, S.; Klärner, F.-G. *Chem. Ber.* **1993**, *126*, 485.
3. Prinzbach, H.; Bingmann, H.; Markert, J.; Fischer, G.; Knothe, L; Eberbach, W.; Brokatzky-Geiger, J. *Chem. Ber.* **1986**, *119*, 589.
4. Prinzbach, H.; Klaus, M. *Angew. Chem.* **1969**, *81*, 289; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 276.
5. Martin, H.-D.; Kaudy, L.; Stusche, D. *Tetrahedron Lett.* **1977**, 3561.
6. LaRochelle, R. N.; Trost, B. M. *Chem. Commun.* **1970**, 1353.
7. Srinivasan, R., Ors, J.A., Brown, K.H., Baum, T., White, L.S., Rosci, A.R., *J. Am. Chem. Soc.* **1980**, *102*, 5297.
8. From the spectroscopic data reported by T. Golz, Dissertation, Ruhr-Universität Bochum, 1991 (research director: F.-G. Klärner) only the data of the most important compounds are given: **5**: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.36$ (m, 2H, 6,8-H, $J_{6,7x}=J_{8,7x}=4.5$ Hz, $J_{6,5}=J_{8,1}=5{,}0$ Hz, $J_{6,4}=J_{8,2}=6.5$ Hz); 1.83 (d, 1H, 7x-H, $J_{7x7n} = 12.0$ Hz); 1.89 (dt, 1H, 7n-H); 2.01 (m, 2H, 1,5-H, $J_{1,2}=J_{5,4}=3.5$ Hz); 4.00 (m, 2H, 2,4-H). ^{13}C-NMR (100.61 MHz, DEPT, $CDCl_3$): $\delta = 20.92$ (CH_2, C-7); 24.16 (CH, C-6,8); 25.37 (CH, C-1,5); 65.96 (CH, C-2,4) IR (film); $\tilde{\nu} = 3060$ cm (Cyclopropyl-H); 2920, 2860 (C-H); 1470 (C-H); 1270, 1180, 1020, 920, 900 (C-O-C), MS (m/e %) = 108 (1.8 , M^+), 79 (100, M^+-CO,-H), **7**: ^{1}H-NMR (400 MHz, $CDCl_3$): $\delta = 1.83$ (dm, 1H, 10x-H, $J_{10x,10n} = 12.0$ Hz, $J_{10x,1} = 1{,}5$ Hz); 1.97 (d, 1H, 10n-H; 2.70 (m, 1H, 1-H, $J_{1,2} = 3.0$ Hz); 2.79 (m, 1H, 4-H, $J_{4,3} = 3.0$ Hz); 3.49 (d, 1H, 6-H, $J_{6,7} = 5.0$ Hz); 3.57 (dd, 1H, 7-H, $J_{7,8} = 6.0$ Hz); 4.21 (m, 2H, 5,8-H); 6.13 (dd, 1H, 2-H, $J_{2,3} = 5{,}5$ Hz); 6.17 (dd, 1H, 3-H). ^{13}C-NMR (100.61 MHz, DEPT, $CDCl_3$): $\delta = 32.29$, 37.55 (2CH, C-1,4); 38.59 (CH_2, C-10); 42.60, 43.73 (2CH, C-6,7); 73.19 (CH, C-5,8); 116.34, 119.60 (2C, 6,7-CN); 132.19, 132.67 (CH, C-2,3). IR (film): $\tilde{\nu} = 3070\ cm^{-1}$ (=C-H), 2220 (C≡N). MS: m/e (%) = 186 (22, M^+), 79 (100, $C_6H_7^+$).
9. The reaction of benzene oxide $\rightleftharpoons$ oxepine (review: Vogel, E., Günther, H. *Angew. Chem.* **1967**, *79*, 429; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 385) with diazomethane CH_2N_2/Cu_2Cl_2 at -70 °C gives 5% 2-oxabicyclo[5.1.0]octa-3,5-diene, 33 % 4-oxabicyclo[5.1.0]octa-2,5-diene (Klein, H., Kursawa, W., Grimme, W., *Angew. Chem.* **1972**, *85*, 624; *Angew. Chem. Int. Ed. Engl.* **1972**, *12*, 580), and 12 % 4H-oxacin **19**. **11** (obtained by 1,3-dipolar cycloaddition of CH_2N_2 to 2-oxabicyclo[3.2.0]hepta-3,6-diene followed by photolysis of the adduct) undergoes a thermal rearrangement to 4-oxabicyclo[5.1.0]octa-2,5-diene which is explained by a sequence of 1,4-electrocyclic ring-opening leading to **20** followed by a [1,6] carbon shift. .Weubel, G., Dissertation, Ruhr Universität Bochum, 1992 (research director: F.-G. Klärner).
10. Schiess, P.; Wisson, M. *Helv. Chim. Acta* **1974**, *57*, 1692.
11. Svenson, T. *Chem. Scr.* **1973**, *3*, 171.
12. ^{1}H NMR signals of **14** were compared with those of bicyclo[3.1.0]hex-2-ene-4-yl acetate; Farenhorst, E. Bickel, A.F. *Tetrahedron Lett.* **1966**, *7* 5911.
13. Review: Adam, W.; Oppenlaender, T. *Angew. Chem.* **1986**, *98*, 659; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 661.
14. A diester-substituted derivative of **18** is known to isomerize to the corresponding derivative of **19** smoothly at 0 °C. Prinzbach; H., Stusche; D., Brenninger, M.; Markert, J. *Chem. Ber.* **1976**, *109*, 2823.
15. Schiess. P.; Wisson. M. *Helv. Chim. Acta* **1974**, *57*, 984.
16. Jackman, J. M.; Sarkis, G. Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1179.
17. Meinwald, J.; Labana, S.S.; Chadha, M.S. *J. Am. Chem. Soc.* **1963**, *85*, 582; Lumb; J.T.; Whitham, G.H.; *J. Chem. Soc.* **1964**, 1189; Meinwald, J.; Labana, S.S., Labana, L.L; Wahl Jr., G.H. *Tetrahedron Lett.* **1965**, 1789; Rey, M.; Dreiding, A.S. *Helv. Chim. Acta* **1965**, *48*, 1985.

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