ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 147 (2002) 109–112

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photocyclization of an isopentafulvene–benzoquinone adduct: a vinylogous Norrish–Yang reaction☆

Axel G. Griesbeck*, Dieter Scheutzow

Institute of Organic Chemistry, University of Cologne, Greinstr. 4, D-50939 Köln, Germany

Received 16 July 2001; received in revised form 29 October 2001; accepted 20 November 2001

Abstract

The Diels–Alder reaction of *N*-methyl-4H-1,2,4-triazoline-3,5-dione (MTAD) with a mixture of isopentafulvenes **2a**,**b** resulted in two 1:1 adducts **3a**,**b** in a 65:35 ratio. The less reactive dienophile benzoquinone gave only one diastereomerically pure pentacyclic 1:2 adduct **4**. The photolysis of **4** initiated a highly regioselective allylic hydrogen transfer reaction and resulted in the formation of the cyclobutanol **5** via an unusual vinylogous Norrish–Yang photocyclization. Prolonged photolysis of **5** gave the supercage molecule **6** via intramolecular photocycloaddition.

Keywords: Diels–Alder reaction; Photoisomerization; Hydrogen transfer; Yang reaction

1. Introduction

During our studies on the synthesis of polycyclopentanoid target molecules using the photo–thermo metathesis route [1], the vacuum flash thermolysis (VFT) of 6-cyclopropylpentafulvenes was discovered as an efficient route to isoindanes [2]. Thermolysis of the structurally comparable 6-oxiranylpentafulvenes was subsequently investigated as potential approach to iridoid products [3]. Unexpectedly, the VFT of oxirane **1** (already used in natural product synthesis [4]) resulted in decarbonylation and the formation of two isomeric isopropenyl cyclopentadienes ("isopentafulvenes") **2a** and **2b** (Scheme 1) in a 64:36 ratio [2]. The cycloaddition reaction of tetracyanoethylene with **2** was already described in the literature [5]. In order to determine the exact product composition of the thermolysis mixture directly after VFT, further cycloadditions were investigated. As a *highly* reactive dienophile, *N*-methyl-4H-1,2,4-triazoline-3,5-dione (MTAD) was used. The cyclopentadiene isomers **2** were trapped at −78 °C and the two Diels–Alder adducts **3a** and **3b** (Scheme 2) were isolated in a 2:1 ratio (93% yield). Thus, MTAD reacts faster in comparison with diene equilibration or the reactivity of MTAD with both dienes is of comparable magnitude. In order to decide on this alternative, we used benzoquinone as a less reactive dienophile.

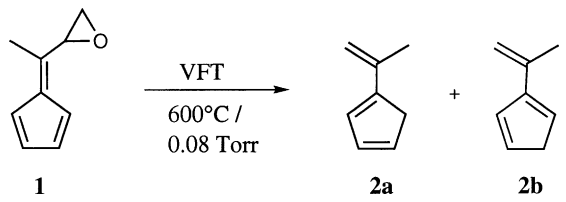
At low temperatures, benzoquinone (used in excess) did not react at all and the reaction mixture had to be warmed to 0 °C. Under these conditions, only one product was formed, the pentacyclic 1:2 adduct **4**. Thus, equilibration of the two isomeric dienes **2a** and **2b** was rapid in comparison with the Diels–Alder reaction of benzoquinone with the more reactive **2b**. Both subsequent Diels–Alder cycloadditions proceeded highly *endo*-selective and resulted in only one diastereoisomeric 1:2 adduct. The relative configuration of this adduct resulted from the analysis of the chemical shifts of the olefinic benzoquinone hydrogenatoms and the coupling constants with the norbornene bridgehead hydrogens. Ultimate proof for the structure of **4** came from its photochemical behaviour: Short-time irradiation of **4** with UV-light ($\lambda = 300 \pm 10$ nm) gave quantitatively the cyclobutanol derivative **5** (Scheme 3).

Further irradiation led to the disappearance of the olefinic signals in the proton NMR and new signals typical for the second cyclobutane ring in the [2+2]-cycloadduct **6** which could be clearly detected from the NMR analysis. Unfortunately, **6** could not be separated from the oligomeric by-products resulting formed from intermolecular photocycloadditions.

☆ Dedicated to Professor Manfred Christl on the occasion of his 60th birthday.

* Corresponding author. Tel.: +49-221-470-3083; fax: +49-221-470-5057.
E-mail address: griesbeck@uni-koeln.de (A.G. Griesbeck).

1010-6030/02/$ – see front matter
PII: S1010-6030(01)00639-6



Scheme 1. Synthesis of the isopentafulvene **2**.

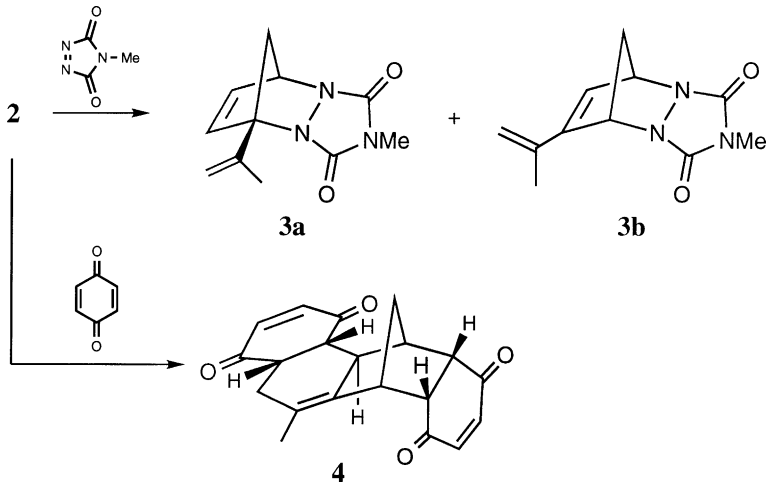
2. Experimental

2.1. General aspects and methods

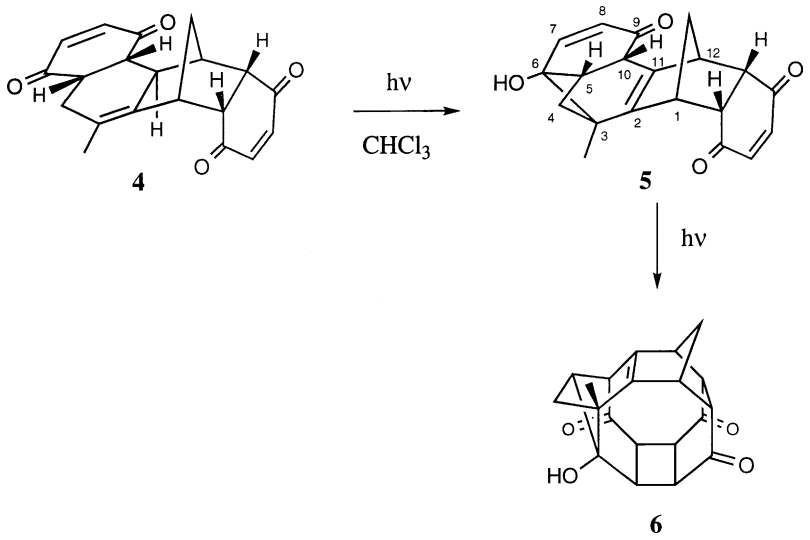
The oxiranylpentafulvene **1** was synthesised following a literature procedure [4]. IR: Perkin-Elmer 1420. ^{1}H NMR: Bruker AC 500 (500 MHz). ^{13}C NMR: Bruker AC 250 (63.4 MHz), carbon multiplicities were determined by DEPT. Column chromatography: silica gel (Merck) 60–230 mesh; petroleum ether (PE, 40–60 °C), ethyl acetate (EA). Combustion analyses: Institute of Inorganic Chemistry, University of Cologne.

2.2. MTAD-adducts *(3a,b)*

Vaccum flash thermolysis at 600–640 °C/0.05 Torr (for conditions see [10]) of 3.12 g (23.3 mmol) of **1** resulted in 1.58 g (64%) of a mixture of cyclopentadienes **2a,b** in a ratio of 65:35. Analogously, 500 mg (3.7 mmol) of **1** was thermolysed and condensed into a trap cooled to −78 °C equipped with a solution of 395 mg (3.6 mmol) of MTAD in 5 ml of chloroform. After completion of the VFT, the dienophile solution was completely discoloured. After evaporation of the solvent, column chromatography (CH_2Cl_2/EA 5:1) gave 734 mg (93%) of a 66:34 mixture of the adducts **3a,b** as a



Scheme 2. Cycloaddition of isopentafulvene **2** with MTAD and benzoquinone.



Scheme 3. Photoisomerization of **4** and photocyclization of **5**.

colourless powder. **3a**: ^{1}H NMR ($CDCl_3$): $\delta = 2.00$ (s, 3H), 2.88 (s, 3H), 3.03 (m, 2H), 5.20–5.31 (m, 3 H), 6.29 (dd, $J = 2.2$, 5.4, 1H), 6.37 (dd, $J = 1.4$, 5.4, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 19.4$ (q), 25.3 (q), 29.5 (s), 53.4 (t), 64.7 (d), 114.9 (t), 130.5 (d), 132.8 (d), 135.9 (s), 154.2 (s), 154.7 (s). **3b**: ^{1}H NMR ($CDCl_3$): $\delta = 1.77$ (s, 3H), 2.15–2.28 (m, 2H), 2.86 (s, 3H), 5.00–5.21 (m, 4H), 5.98 (s, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 19.6$ (q), 25.5 (q), 48.4 (t), 64.1(d), 65.0 (d), 81.3 (s), 117.3 (t), 121.2 (d), 138.2 (s), 154.5(s), 155.2(s).

2.3. Benzoquinone adduct (4)

To a precooled (0 °C) solution of 800 mg (7.5 mmol) of a mixture of **2a,b** in 20 ml of acetone was added a solution of 1.63 g (7.5 mmol) of benzoquinone in 30 ml of acetone. After stirring for 60 mm at 0 °C, the solvent was evaporated and the residue recrystallysed from ethanol resulting in 490 mg (20%) of **4** as a colourless powder, m.p. 170–171 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.42$ (d, $J = 10.2$, 1H), 1.57 (s, 3H), 1.71 (d, $J = 10.2$, 1H), 1.80 (m, 2H), 1.97 (dd, $J = 6.1$, 16.4, 1H), 2.19 (ddd, $J = 7.8$, 8.4, 16.4, 1H), 2.98 (m, 1H), 3.06 (m, 2H), 3.20 (m, 1H), 3.46 (m, 1H), 6.52 (s, 2H), 6.57 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 16.9$ (q), 31.6 (t), 38.4 (d), 39.2 (t), 40.9 (d), 44.6 (d), 46.9 (d), 47.3 (d), 48.7 (d), 50.5 (d), 125.3 (s), 134.9 (s), 139.2 (d), 140.6 (d), 141.2 (d), 141.6 (d), 197.9 (s), 198.9 (s), 199.6 (s), 200.5 (s). –$C_{20}H_{18}O_4$ (322.3): calcd. C 74.52, H 5.63; found C 74.45, H 5.77.

2.4. Photolysis of the benzoquinone adduct

A solution of 200 mg (0.62 mmol) of **4** in 20 ml of chloroform was irradiated for 8 h at 10 °C in a pyrex cuvette with a 75 W fluorescence lamp emitting at 300 ± 10 nm. After evaporation of the solvent and column chromatography, 164 mg (82%) of **5** resulted as a yellowish oil. ^{1}H NMR ($CDCl_3$): $\delta = 0.92$ (d, $J = 7.0$, 1H), 0.98 (s, 3H), 1.01 (d, $J = 7.0$, 1H), 1.45 (d, $J = 4.4$, 1H), 1.64 (d, $J = 7.3$, 1H), 1.86 (d, $J = 1.6$, 1H), 2.26 (m, 1H), 2.76 (d, $J = 4.3$, 1H), 2.81 (d, $J = 4.3$, 1H), 2.95 (s, br, OH, 1H), 3.04 (d, $J = 7.3$, 1H), 3.24 (d, $J = 1.3$, 1H), 6.02 (dd, $J = 1.3$, 9.8, 1H), 6.49 (s, 2H), 7.18 (d, $J = 9.8$, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 21.2$ (q), 35.2 (t), 38.7 (t), 41.6 (d), 41.9 (d), 43.0 (d), 49.7 (d), 57.0 (d), 61.5 (d), 77.3 (s), 80.3 (s), 94.4 (s), 95.5 (s), 132.9 (d),141.9 (d), 142.0 (d), 148.8 (d), 198.9 (s), 199.5 (s), 199.6 (s). $C_{20}H_{18}O_4$ (322.3): calcd. C 74.52, H 5.63; found C 74.13, H 5.56. Irradiation of the sample for additional 24 h leads to complete disappearance of the olefinic signals in the ^{1}H NMR.

3. Results and discussion

The structure of the Norrish–Yang product **5** was proven by a complete 2D-NMR analysis. Significant proton signals were detected for the cyclobutane hydrogen H-4 at 0.92 and 1.01 ppm and the enone group at 6.02 ppm (H-8) and 7.18 ppm (H-7). Only marginal changes in the NMR spectra were observed for the“right side “of the hexacyclic photoproduct where only little structural changes occurred. The comparison of the ^{13}C NMR signals of the relevant carbon positions also revealed the proposed structure (Table 1).

Table 1
Characteristic ^{13}C NMR chemical shifts for **4** and **5**

	4	**5**
C-1	50.5	61.5
C-2	125.3	94.4
C-3	134.9	77.3
C-4	31.6	35.2
C-5	46.9	41.9
C-6	197.9	80.3
C-7	141.2	148.8
C-8	141.6	132.9
C-9	198.9	198.7
C-10	47.3	49.7
C-11	38.4	95.5
C-12	48.7	57.0

The 2:1 Diels–Alder adduct **4** has the structural feature of a tetrahydronaphthoquinone, a class of substrates which has been thoroughly investigated with respect to solution and solid-state photochemistry by Scheffer and Pokkuluri [6]. Compared with these results, the photoisomerization of **4** is unusual in the sense that it does not follow the typicial tetrahydronaphthoquinone photochemistry, which is dominated either by β-hydrogen abstraction initiated by one of the quinone carbonyl groups or by γ-hydrogen abstraction initiated by the quinone carbon–carbon double bond. Classical Norrish-type II initiated cyclisation of 1-hydroxytetramethylene biradicals (Yang cyclisation) [7] has yet not been described for these substrates. In the case of the **4** → **5** isomerization, a vinylogous Norrish–Yang reaction occurred, i.e. hydrogen atom transfer is initiated from an allylic CH position and radical combination to give a rearranged 2-vinylcyclobutanol terminates the reaction. Thus, this reaction follows a sequence of hydrogen transfer and radical combination as shown in Fig. 1.

A thermal analogue to this sequence is the ene reaction of unsaturated carbonyl compounds, a versatile method for the synthesis of cyclopentanols and higher homologues [8]. The hydrogen (H1 in Figs. 2 and 3) selectively abstracted by the carbonyl oxygen O1 despite of the larger O–H distance in comparison with H1–O2.

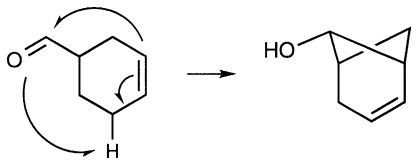


Fig. 1. Vinylogous Norrish–Yang photocyclization.

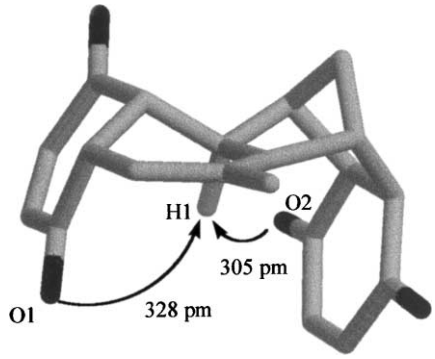


Fig. 2. PM3 calculated structure of **4**.

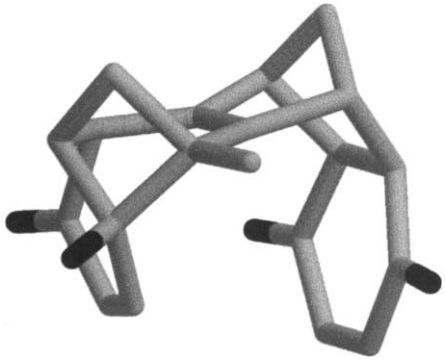


Fig. 3. PM3 calculated structure of **5**.

The optimal OH-distance for Norrish II hydrogen transfer is ca. 2.7 Å and the out-of-plane angle ω of the hydrogen with respect to the plane containing the carbonyl *n*-orbital can deviate from its optimal value of 0 °C by as much as 50–60 °C[9]. Molecular dynamics calculations indicate that in **4** the flexibility of the "left" benzoquinone part is much higher allowing the approach of O1 and H1 necessary for interaction in the triplet excited state. Furthermore, the angle ω for H1–O2 is ca. 90 °C and thus unfavourable for H transfer. The hexacyclic compound **5** is photolabile under the irradiation conditions and slowly bleaches with formation of insoluble material. From the disappearance of the olefinic NMR signals from the enone and enedione moieties and comparison with other cage compounds originating from benzquinone/cyclopentadiene adducts [1], we concluded that [2+2]-photocycloaddition had occurred, in part intramolecular to give the supercage product **6** together with intermolecular reactions leading to oligomeric products.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

[1] A.G. Griesbeck, Chem. Ber. 123 (1990) 549.
[2] A.G. Griesbeck, K. Peters, E.-M. Peters, H.G. von Schnering, Angew. Chem. 102 (1990) 801;
A.G. Griesbeck, K. Peters, E.-M. Peters, H.G. von Schnering, Angew. Chem. Int. Ed. Engl. 29 (1990) 803.
[3] T.-L. Ho, Carbocycle Construction in Terpene Synthesis, VCH, Weinheim, 1988.
[4] (a) K. Antczak, J.F. Kingston, A.G. Fallis, Tetrahedron Lett. 25 (1984) 2077;
(b) K. Antczak, J.F. Kingston, A.G. Fallis, Can. J. Chem. 62 (1984) 2451.
[5] D.B. Knight, R.L. Hartless, D.A. Jarvis, J. Org. Chem. 37 (1972) 688.
[6] J.R. Scheffer, P.R. Pokkuluri, in: V. Ramamurthy (Ed.), Photochemistry in Organised and Constrained Media, VCH, New York, 1991, p. 188.
[7] (a) N.C. Yang, D.-D.H. Yang, J. Am. Chem. Soc. 80 (1958) 2913;
(b) P.J. Wagner, B.-S. Park, Org. Photochem. 11 (1991) 227;
(c) A.G. Griesbeck, H. Heckroth, J. Lex, J. Chem. Soc., Chem. Commun. (1999) 1109.
[8] (a) M. Bortolussi, R. Bloch, J. M. Conia, Bull. Soc. Chim. Fr. (1975) 2722;
(b) C. Aubert, J.-P. Begue, D. Bonnet-Delpon, Chem. Lett. (1989) 1835;
(c) A. Srikrishna, K. Krishnan, S. Vankateswarlu, J. Chem. Soc., Chem. Commun. (1993) 143.
[9] H. Ihmels, J.R. Scheffer, Tetrahedron 55 (1999) 885.
[10] A.G. Griesbeck, Synthesis (1990) 144.