Tetrahedron 69 (2013) 10445–10449

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Photooxidation of unhindered triarylcorroles

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ARTICLE INFO

Article history:
Received 21 June 2013
Received in revised form 18 September 2013
Accepted 30 September 2013
Available online 5 October 2013

Keywords:
Biliverdin
Corrole
Degradation
Isocorrole
Photooxidation

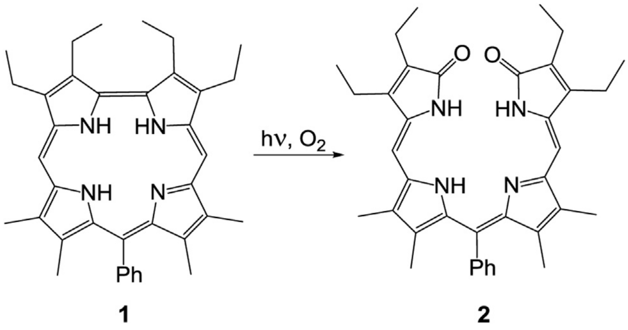
ABSTRACT

Photooxidation of 5,10,15-triphenylcorrole and 5,10,15-tris(*p*-methoxy)phenylcorrole was performed leading to a mixture of isocorroles and ring-opened products, resulting from attack of dioxygen at 5- (15-) and 10-*meso* position.

1. Introduction

The increasing interest in corrole macrocycles observed over last decades is connected with their wider synthetic availability,[1–3] as well as possible applications in various fields including catalysis, gas sensing, chromophores for light energy conversion and singlet oxygen generation.[4–6] Utilization of these compounds in photoactive devices is warranted by their stability. A stepwise degradation of corroles in solution in the presence of light and air was manifested by a systematic lowering of Soret band intensity in UV–vis spectra.[7,8] Guilard et al. put forward the first proposal of a structure of the degradation product of photooxidation of 2,3,17,18-tetraethyl-7,8,12,13-tetramethyl-10-phenylcorrole **1** (Scheme 1).[9] A biliverdin derivative **2** was obtained in 24% yield and characterized by ^{1}H NMR and IR spectroscopy, mass spectrometry and elemental analysis, which were in general agreement with an intuitive assumption that pyrrole–pyrrole (C_1–C_{19}) bond was attacked by dioxygen molecule. No other reaction products were isolated. Opening of the corrole ring by breaking of the C_α–C_α bond was also postulated by Paolesse et al. for photooxidation of β-octaalkylcorrole with a porphyrin attached to a 10-position.[10]

A systematic mass spectrometry study on the decomposition pathways of *meso*-triarylcorroles bearing various substituents in phenyl rings led to the identification of isocorroles and ring-opened tetrapyrroles as photooxidation products.[11] On a preparative scale, an acetonitrile solution of corrole **3** with the 5 and 15 positions protected by mesityl substituents was exposed to sunlight for 60 h. Three major products: 10-isocorrole **4** and two biliverdin derivatives **5**, **6** (differing only by the orientation of the terminal pyrrolone) derived from dioxygen attack on *meso*-C_{10} carbon atom were isolated from the reaction mixture (Scheme 2).



Scheme 1. Photooxidation of 10-phenyl-substituted octaalkylcorrole.[9]

Substitution of the macrocycle strongly influences its reactivity, for example, 5,10,15-tris(pentafluorophenyl)corrole stirred at room temperature under ambient light and air slowly converted to 3,3′-linked dimer and 3,3′,17′,3″-trimer.[12] Corrole opening by different oxidants has been also described. Zinc complex of an open-chain of tetrapyrrole **7** (Fig. 1) was formed in minor quantities upon bromination of germanium(IV) 5,10,15-triphenylcorrole.[13] A biliverdin analogue **8** (Fig. 1) was identified as a by-product of triarylcorrole reaction with 4-amino-4*H*-1,2,4-triazole.[14] Ring opening at C_{10}

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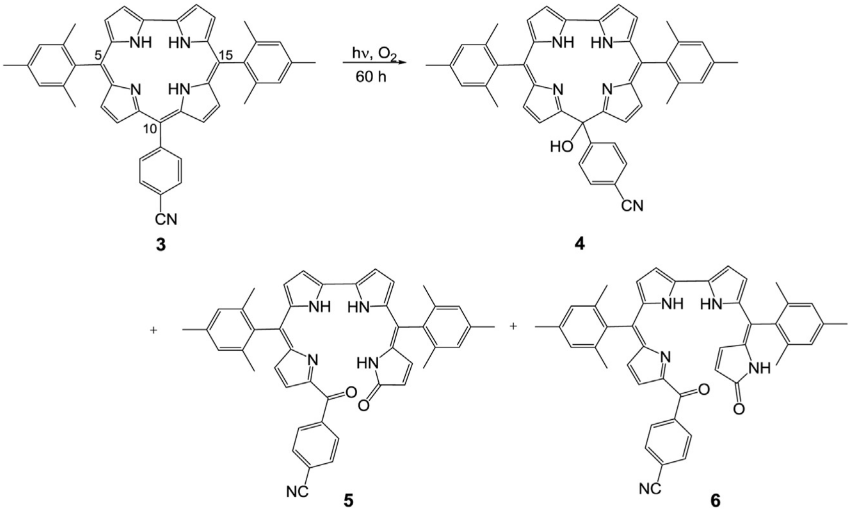
http://dx.doi.org/10.1016/j.tet.2013.09.090



Scheme 2. Photooxidation of 5,15-protected triarylcorroles.[11]

combined with an extrusion of the *meso* carbon bearing a *para*-nitrophenyl substituent was also observed upon conversion of triarylcorrole to a corresponding porphyrin.[15]

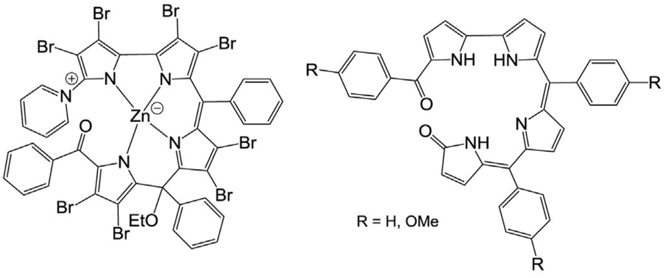


Fig. 1. Ring-opened by-products of corrole oxidation.[13,14]

Other pathways of corrole oxidation have been reported, including isocorrole formation by DDQ treatment[16,17] or demetallation,[18,19] and oxidative dimerization of 5,10,15-tris(pentafluorophenyl)corrole with formation of β–β′ bond(s) upon heating in 1,2,4-trichlorobenzene.[20]

All these examples demonstrate the strong dependence of corrole substitution on the pathways of oxidative degradation, and the fact that the structures of possible reaction products cannot be easily predicted. Surprisingly, any systematic studies on the photooxidation of unhindered, A_3-type corroles have not been reported. In this contribution, we describe the photooxidation of triphenylcorrole **9a** and tris(4-methoxyphenyl)corrole **9b** and the identification of tetrapyrrolic products of this reaction.

2. Results and discussion

2.1. Photooxidation of triarylcorroles

Triarylcorroles **9a**, **9b** were dissolved in dichloromethane and stirred for 3 h with simultaneous irradiation with a 60 W tungsten lamp, while a stream of air was passed slowly through the solution. Reaction time was optimized in order to ensure the complete degradation of corroles, but without formation of subsequent photochemical reaction products (vide infra). As a consequence, ca. 10–15% of unreacted compounds **9a** and **9b** were recovered as a first chromatographic fraction, which was followed by a mixture of isocorroles **10** and **11**, and more polar fractions containing linear tetrapyrroles **12** and **13** (Scheme 3). Minor amounts of smaller degradation products, a diacylpyrrole and dipyrrole derivative, were also detected by ^{1}H NMR spectroscopy in chromatographic fractions, but they were not isolated in a pure form. A significant amount of the starting corrole was converted to dark products, which remained on the top of silica column even when eluent polarity was significantly increased up to 20–30% methanol in dichloromethane.

Photooxidation of both corroles yielded two isomeric isocorrole products in 5–11% overall yield. In the case of the phenyl derivatives, these isomers were formed in comparable amounts (**10a**:**11a**=1:1.1), while in the case of the *p*-methoxy-substituted compounds, the 10-isocorrole predominated (**10b**:**11b**=1:3.8). Chromatographic separation of the isomers was hampered by their similar R_f values and was therefore not achieved. Identification of isocorroles was based on mass spectrometry data and NMR (^{1}H, ^{13}C) spectroscopy measurements. In the ESI mass spectra of the isomeric mixtures, an apparent molecular ion $[M+H]^+$ was observed together with a dehydroxylation product $[M-OH]^+$. Characteristic NH signals (one for compounds **11**, and two for **10**) at ca. 16 ppm were found in the ^{1}H NMR spectra. The number of pyrrole signals in the 6–7 ppm region reflected the symmetry of the molecules, and the broad signals of −OH groups were localized in 2.6–2.8 ppm region. A diagnostic ^{13}C NMR resonance derived from a sp^3 *meso* carbon was detected at 73–76 ppm, and its correlation with the respective aryl *ortho* proton was observed in the HMBC maps. Compounds **10a** and **11a** were identical with those previously prepared and characterized by Mandoj et al. in the course of the demetallation of corrole complexes.[18]

Linear isomeric tetrapyrroles **12** and **13** were identified through the analysis of their NMR characteristics (^{1}H, ^{13}C, and correlation spectra) and MS measurements. In the ^{1}H NMR spectra, eight pyrrole resonances were located in the 6–8 ppm range as expected for the loss of macrocyclic aromaticity due to ring opening. A characteristic doublet at ca. 8 ppm for the *ortho*-phenyl proton of the terminal benzoyl substituent was observed in all spectra. Two carbonyl resonances were found in the ^{13}C NMR spectra at 171–173 ppm and 182–184 ppm and attributed to the pyrrolone and benzoyl fragments, respectively.

A green compound **12** was formed in ca. 10% yield by dioxygen attack on the C_4–C_5 bond of the starting corrole, and thus contains bipyrrole as a terminal unit. One pair of pyrrolic resonances was