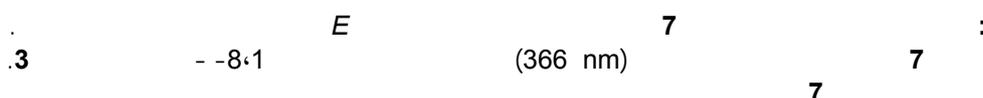# Synthesis and Crystal Structure of Overcrowded Non-photochromic Organometallic Fulgide

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.   *E*   **7**   :
.**3**   – –8،1   (366 nm)   **7**
.   **7**

ABSTRACT: Pure *E*-isomer overcrowded organometallic fulgide **1** was obtained by using successive Stobbe condensations between ketones and succinate diester. Upon irradiation with UV light at (366 nm) it did not cyclise photochemically to the 1,8a-dihydronaphthalene derivative (1,8a-DHN) **8**. The structure of **7** was confirmed by X-ray crystallographic analysis.

KEYWORDS: Fulgide, Stobbe Condensation, Organometallic, Crystal Structure.

1.   Introduction

Fulgides with aryl ring undergo ring-closure photochemically to give highly coloured tricyclic dihydronaphthalene derivatives (Heller 1978). It was found that the preferred isomer was the *E*-isomer in sterically-hindered fulgide systems (Hart and Heller 1972; McCabe *et al.* 1993; Liang *et al.* 2001). McCabe *et al.* (1993) synthesized the first organometallic fulgide **1,** which was obtained as *E*-isomer **1**. Irradiation of **1** underwent *E/Z* isomerization to *Z*-isomer **2** rather than ring-closure, despite the introduction of donating groups on the ferrocenyl moiety Scheme 1.
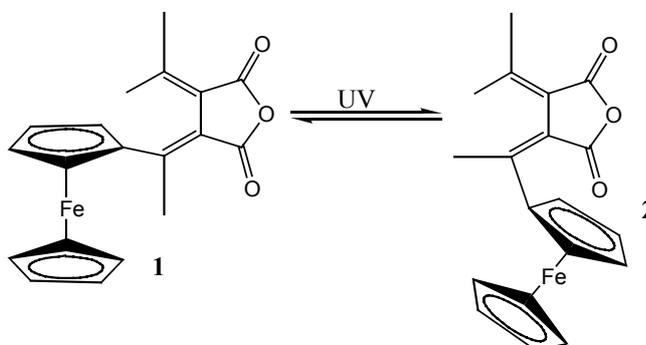
Scheme 1: *E/Z* isomerization of fulgide 1.

In the present work diphenylidene was introduced to the system to investigate whether or not photocyclization would occur, according to electrocyclization reaction, in agreement with Woodward-Hofmann rules (Yokoyama 2000).

2. Experimental

General: Melting points were recorded on a Gallenkamp melting point apparatus and were uncorrected. NMR spectra were obtained in CDCl$_3$ on a Jeol 400 MHz with TMS as internal reference; chemical shifts were expressed in δ (ppm). Irradiation of the prepared fulgide in toluene at 366 nm for 48 hrs was carried out, using UV lamp (UV GL-58, 254/366 nml lamp, 50/60 Hz), while UV–Visible double beam spectrophotometer (Shimadzu UV-1601PC) was used to follow up the irradiation effect.

Dimethyl (diphenylmethylene)succinate 4: A mixture of benzophenone (18.2 g, 0.1 moles), dimethyl succinate (17.5 g, 0.12 moles) and potassium *t*-butoxide (12 g, 0.1 moles) in toluene (200 ml) was stirred for 6 hours. Work-up produced the half ester, which was esterified to give the diester as yellow crystals (17 g, 55% yield) m.p. 78-79ºC. ^{1}H-nmr: 3.46 (2H, s, CH$_2$ proton), 3.45 (3H, s, CH$_3$O), 3.70 (3H, s, CH$_3$O), 7.10-7.40 (10H, m, aromatic proton).

Ferrocenylethylidene(diphenylidene)succinic anhydride 7: Stobbe condensation on an equimolar basis of dimethyl (diphenylmethylidene) succinate (10 g, 0.03 moles) and ferrocene (7.5 g, 0.03 moles) in toluene (200 ml) in the presence of potassium *t*-butoxide, followed by hydrolysis of the half ester gave the diacid, which cyclised with acetyl chloride. The solvent and acetyl chloride were removed and the residue was dissolved in dichloromethane and chromatographed on silica gel to give the fulgide **7** as black crystals from dichloromethane and petroleum ether (4.5 g, 28%). m. p. 234-235ºC ^{1}H-nmr: 2.65 (3H, s, CH$_3$), 4.34 (5H, s, Cp' and 1H, s, Cp), 4.66 (3H, s, Cp), 3.70 (3H, s, CH$_3$O), 7.13-7.46 (10H, m, aromatic proton).Found: C, 73.07; H, 4.39%. C$_{29}$H$_{22}$O$_3$Fe requires: C, 73.42; H, 4.64%. m/z, 474.

2.1 X-Ray analysis

A dark purple crystal with dimensions 0.483 x 0.260 x 0.188mm^3 was placed and optically centered on the Bruker SMART CCD system at –80°C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans (25 frames/series) that were well distributed in reciprocal space. Data frames were collected [MoKα] with 0.3° wide ω-scans, 30 seconds/frame, 606 frames per series. Five complete series were collected, including an additional partial, first 160 frames, run of the first series for decay purposes, with a crystal to detector distance of 4.94cm, thus providing a complete sphere of data to $2\theta_{max}$=55°. A total of 30967 reflections was collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS (Blessing 1995 and Sheldrick 1996) with 5041 unique [R(int)=0.0273].

3. Results and Discussion

Stobbe condensation of benzophenone and dimethyl succinate in the presence of potassium *t*-butoxide in toluene and subsequent methylation of the condensation product gave dimethyl (diphenylmethylene)succinate 4. A second Stobbe condensation using acetyl ferrocene yielded the half-ester, which was hydrolysed and cyclised using acetyl chloride, to afford solely fulgide 7 as dark purple crystals in 30% yield (Scheme 2).

Irradiation of fulgide **7** reveals no changes in wavelengths of absorption bands located at λ$_{max}$ 392 and 544 nm ε 11300, 3940 dm^3. ml^{-1}. cm^{-1} respectively. This may indicate that there is neither *E/Z* isomerisation, nor electrocyclic ring closure taking place in this specific fulgide, as normally seen in simple fulgides (Yokoyama 2000) (Scheme 3):

The structure and stereochemistry of fulgide **7** was confirmed by X-ray crystallographic analysis which is shown in Figure 1. Of particular interest in this fulgide are the following features:

- The phenyl rings and the ferrocenyl moiety are rotated from the plane of the anhydride ring.
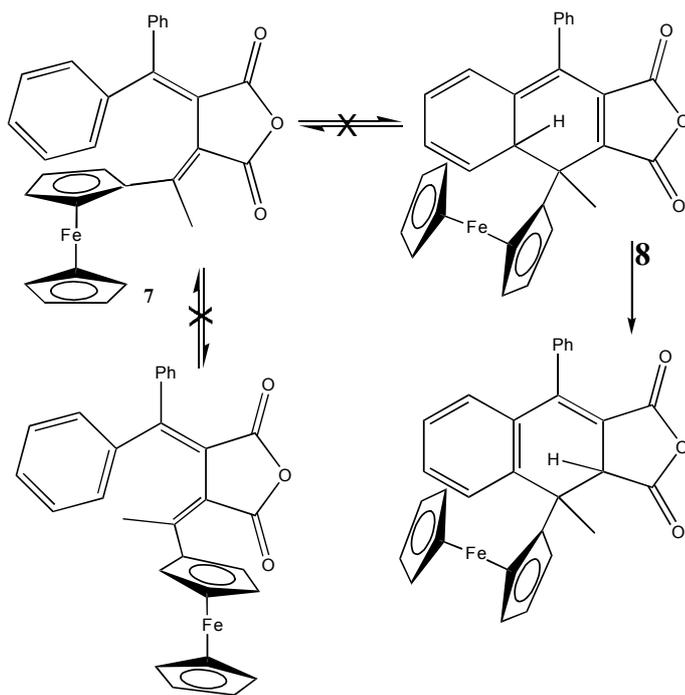- The angle CT2-Fe-CT1 is 177.46(8) and is less than the expected by 2.54°.

- The single bond C11-C12 (1.509 Å) is longer than the single bond C10-C11 (1.457 Å), while the single bonds C17-C18 and C17-C24 have almost the same length 1.489 and 1.484 Å, respectively.
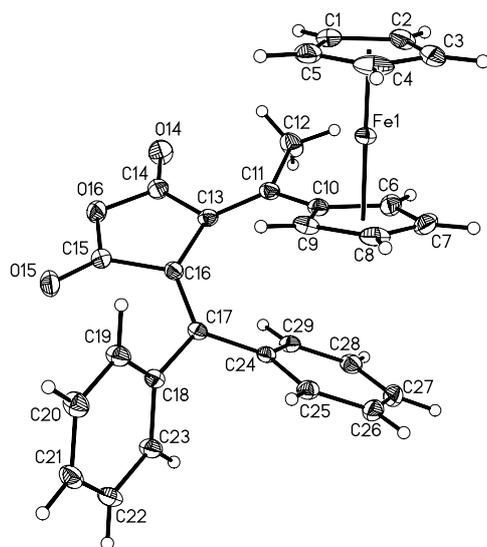
Selected bond lengths and angles are given in Table 1.
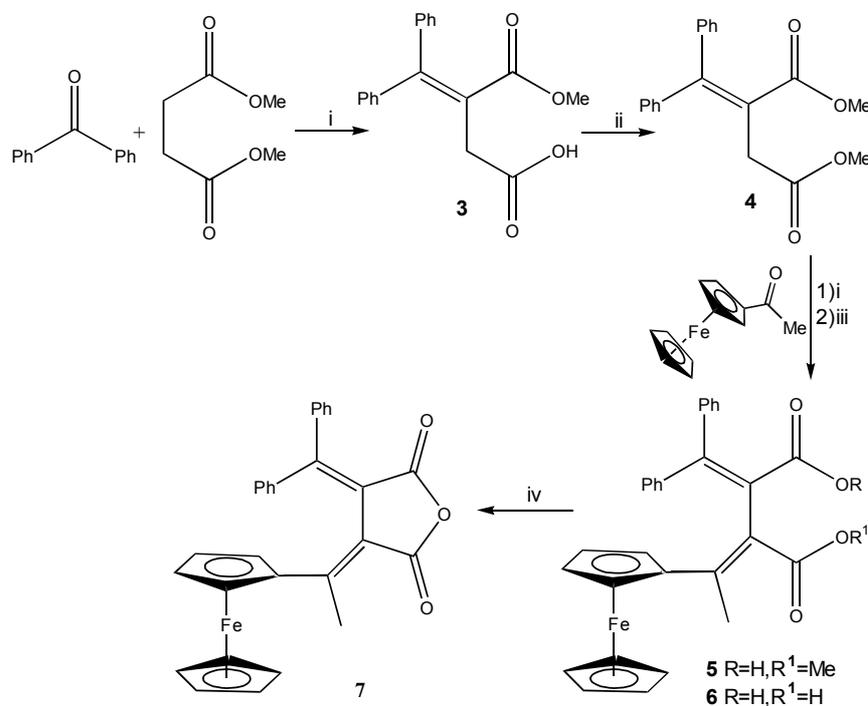
Scheme 2 : Reagents: i=*t*-ButOK, toluene, ii=MeOH, H$^+$, iii=KOH, iv=CH$_3$COCl.

Scheme 3: Irradiation of **7** shows neither *E/Z* isomerization, nor ring closure**.**

Figure 1. The molecular structure of **7** with the atom-numbering scheme. Hydrogen atoms are drawn as circles of arbitrary small radii for clarity.

Table 1 : Selected bond lengths (Å) and bond angles (º) for fulgide **7**.

Fe(1)-CT2	1.647(2)
Fe(1)-CT1	1.661(2)
C(10)-C(11)	1.457(2)
C(11)-C(13)	1.371(2)
C(11)-C(12)	1.509(2)
C(13)-C(16)	1.474(2)
C(16)-C(17)	1.367(2)
CT2-Fe(1)-CT1	177.46(8)
C(9)-C(10)-C(11)	128.40(15)
C(13)-C(11)-C(10)	123.08(14)
C(13)-C(11)-C(12)	120.29(15)
C(10)-C(11)-C(12)	116.63(14)
C(11)-C(13)-C(16)	131.62(14)
C(16)-C(13)-C(14)	105.84(13)
C(17)-C(16)-C(13)	130.84(14)
C(17)-C(16)-C(15)	121.73(14)
C(16)-C(17)-C(24)	121.91(13)
C(16)-C(17)-C(18)	122.11(14)

Structural determination and Refinement: All crystallographic calculations were performed on a Personal computer (PC) with dual Pentium 450MHz processors and 256MB of extended memory. The SHELXTL (Sheldrick 1994) program package was now implemented, XPREP, to determine the probable space group and set up the initial files. System symmetry and systematic absences

indicated the non-standard centrosymmetric space group P2$_1$/n (no.14). The structure was determined by direct methods with the successful location of nearly all atoms using the program XS (Sheldrick 1990). The structure was refined with XL (Sheldrick 1993). After the initial refinement difference-Fourier cycle, additional atoms were located and input. After several of these refinement difference-Fourier cycles, all of the atoms were refined isotropically, then anisotropically. Hydrogen atoms were located directly from difference-Fourier maps and input; these atoms were freely refined. Centroids of the Cp rings were calculated. The final structure was refined to convergence [$\Delta/\sigma \leq 0.001$] with $R(F)$=3.91%, $wR(F^2)$=9.52%, GOF=1.060 for all 5041 unique reflections [$R(F)$=3.30%, $wR(F^2)$=8.87% for those 4386 data with $F_o > 4\sigma(F_o)$]. A final difference-Fourier map was featureless indicating the structure is therefore both correct and complete.

The function minimized during the full-matrix least-squares refinement was $\Sigma w(F_o^2 - F_c^2)$ where $w=1/[\sigma^2(F_o^2) +(0.0517*P)^2 +1.0474*P]$ and $P=(\max(F_o^2,0)+2*F_c^2)/3$. An empirical correction for extinction was attempted but found to be negative and therefore not applied.

Crystal data for fulgide 7

Empirical formula:	*C$_{29}$ H$_{22}$ Fe O$_3$*
Formula weight	474.32
Temperature	193(2) *K*
Wavelength	0.71073 *Å*
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 9.6446(10) *Å* α= 90°.
	b = 12.0427(12) *Å* β= 90.183(2)°.
	c = 19.1244(19) *Å* γ = 90°.
Volume	2221.2(4) *Å*
Z	4
Density (calculated)	1.418 Mg/m^3
Absorption coefficient	0.709 mm^{-1}
F(000)	984
Crystal size	0.13 x 0.210 x 0.424 mm^3
Theta range for data collection	2.00 to 27.50°.
Index ranges	-12<=h<=12, -15<=k<=15, -24<=l<=24
Reflections collected	30967
Independent reflections	5041 [*R(int)* = 0.0273]
Completeness to theta = 27.50°	99.0 %
Absorption correction	*SADABS*
Max. and min. transmission	1.000000 and 0.895124
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5041 / 6 / 392
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	*R1* = 0.0330, *wR2* = 0.0887 [4386 Data]
R indices (all data)	*R1* = 0.0391, *wR2* = 0.0952
Largest diff. peak and hole	0.351 and -0.248 e.

4. Acknowledgements

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