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Formic acid oxidatively cleaves 1,2,3,4-tetraaryl-2-butene-1,4-diones to 1,2-diaryl-1,2-ethanediones under microwave irradiation

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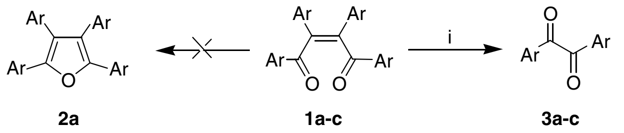
Abstract—Formic acid oxidatively cleaves 1,2,3,4-tetraaryl-2-butene-1,4-diones (1,2-aroylstilbenes) to 1,2-diaryl-1,2-ethanediones (benzils) under microwave irradiation. Mechanistic probing revealed that formic acid incorporates one of its oxygen atoms into benzil.

Formic acid (HCOOH) is a versatile organic compound. It is well known as a natural product[1] and as a one-carbon source in organic synthesis.[2] Furthermore, formic acid has found extensive use as a reducing agent in organic functional group transformations.[2,3] Under appropriate conditions it decomposes to carbon dioxide and hydrogen and the generated hydrogen can be used, under transfer hydrogenation conditions, for the reduction of a wide variety of functional groups.[2] However, formic acid by itself has not been known to oxidize organic compounds, even though performic acid, which is a combination of formic acid and hydrogen peroxide, is a well-known oxidizing agent.[4] In this Letter, we report an unusual and hitherto unknown, oxidizing property of formic acid. We found that it oxidatively cleaves 1,2,3,4-tetraaryl-2-butene-1,4-diones (1,2-aroylstilbenes) to 1,2-diaryl-1,2-ethanediones (benzils) under microwave (MW) irradiation.

Recently, we described a facile MW-mediated synthesis of a range of di- and triarylfurans from di- and triaryl-2-butene-1,4-diones, respectively, with formic acid, Pd/C in the presence of a catalytic amount of sulfuric acid.[5] In continuation of this work, we attempted the synthesis of 1,2,3,4-tetraphenylfuran **2a** from the readily available *Z*-1,2,3,4-tetraphenyl-2-butene-1,4-dione (dibenzoylstilbene) **1a**.[6] Thus, the MW-mediated reaction of *cis*-dibenzoylstilbene **1a** with formic acid in the presence of a catalytic amount of Pd/C and sulfuric acid was anticipated to provide the desired 2,3,4,5-tetraphenylfuran **2a** as shown in Scheme 1. However, and surprisingly, the reaction furnished 1,2-diphenyl-1,2-ethanedione (benzil) **3a** in nearly quantitative yield as the only product (Scheme 1). The formic acid mediated oxidative cleavage of **1a** to **3a** took place even without Pd/C.[7] Clearly, in the present case, formic acid was behaving as an oxidizing agent, that is, oxidatively cleaving the olefin moiety in **1a**.

To test the generality of this unusual oxidative cleavage, we conducted the reaction of substituted dibenzoylstilb-



1a, **3a**: Ar = C_6H_5
1b, **3b**: Ar = 4-ClC_6H_4
1c, **3c**: Ar = 4-$CH_3C_6H_4$

Scheme 1. Reagents and conditions: (i) 85% HCOOH, concd H_2SO_4 (cat), MW, 2 min, 76–96%.

Keywords: Formic acid; Oxidation; Microwave; Diaroylstilbene; Benzil.

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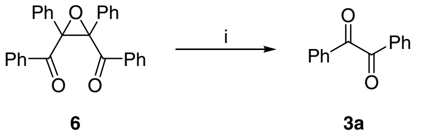
Table 1. Reaction of 2-butene-1,4-diones **1a–c** with the formic acid in the presence of concd sulfuric acid (cat) under MW irradiation

Entry	Ar	Dione	Benzil	Time (min)	Power (W)	Yield[a] (%)
1	C_6H_5	**1a**	**3a**	2	200	96
2	C_6H_5	***E*-1a**	**3a**	2	180	86
3	4-ClC_6H_4	**1b**	**3b**	2	180	88
4	4-$CH_3C_6H_4$	**1c**	**3c**	3	180	76

[a] Isolated yield after column chromatography, no other product was isolated from the reactions.



Scheme 2. Reagents and conditions: (i) 85% HCOOH, concd H_2SO_4 (cat), MW, 0.5 min, 97%.

enes, having electron withdrawing Cl (**1b**) and electron donating Me (**1c**) groups on the aryl rings (Scheme 1 and Table 1). In both cases, only benzil derivatives **3b–c** were obtained in very good yields, and no traces of furan derivatives **2b–c** could be detected. Similarly, the *E*-isomer (***E*-1a**) of *Z*-1,2,3,4-tetraphenyl-2-butene-1,4-dione **1a**[8] was also subjected to MW irradiation with formic acid. In this case also, facile transformation to benzil **3a** occurred.

Next, we sought to find out if the MW-mediated cleavage reaction was a mere reflection of thermal conditions. Therefore, ene-dione **1a** and formic acid were heated in an oil bath. In this case the starting material **1a** was recovered unchanged even after refluxing for 2 h. Therefore, we believe that MW superheating is a necessary condition for this reaction. Since, formic acid failed to cleave 1,2,4-triphenyl-2-butene-1,4-dione,[9] it appears that the steric hindrance encountered in 1,2,3,4-tetraaryl-2-butene-1,4-diones **1a–c** is primarily responsible for the change of the course of the reaction from furan formation to oxidative cleavage.

A possible mechanism for this transformation is given in Figure 1. Since two-electron-withdrawing benzoyl groups flank the olefin in **1**, conjugate addition of a formate anion could lead to an intermediate **4.** This intermediate could react with molecular oxygen to generate **5**, which decomposes into two units of benzil **3**.[10] In an alternative possible mechanism, atmospheric oxygen could add to the double bond in a [2+2] fashion followed by cyclo-reversion in a metathesis manner to generate two benzil units.

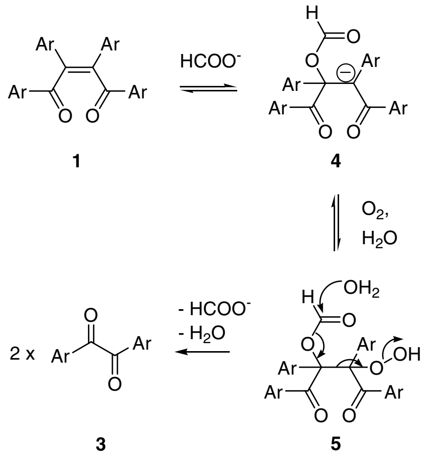


Figure 1.

To test if molecular oxygen in the atmosphere or dissolved oxygen in the medium was responsible for this oxidative cleavage through [2+2] cycloaddition, followed by [2+2] cyclo-reversion (metathesis), the cleavage reaction was performed in an oxygen rich polyethylene glycol (PEG-200) medium without formic acid. There was no change in the starting materials even after exposure to MW for 10 min. Thus, formic acid is necessary for the conversion. Next, a reaction was performed with ^{18}O rich formic acid (48%). From this reaction we isolated benzil, which had 25% incorporation of the ^{18}O label,[11] which confirmed the role of formic acid in the cleavage reaction. The MW-mediated transformation of **1a** to benzil **3a** took place in formic acid alone, that is, without H_2SO_4, but in low yield (39%). Interestingly, when we subjected the epoxide[12] **6** to MW irradiation in formic acid, benzil **3a** was formed in quantitative yield within 30 s (Scheme 2).

In conclusion, we have described an interesting, unusual oxidative cleavage of diaroylstilbenes to benzils with formic acid under MW irradiation.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.05.004.

References and notes

1. Reutemann, W.; Kieczka, H. In *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed.; VCH: Weinheim, 1983; Vol. A12, pp 13–33.
2. Gibson, H. W. *Chem. Rev.* **1969**, *69*, 673–692.
3. (a) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129–179; (b) Brieger, G.; Nestrick, T. J. *Chem. Rev.* **1974**, *74*, 567–580.
4. Yur'Eu, V. M.; Pravednikov, A. N.; Medvedev, S. S. *J. Polym. Sci.* **1961**, *55*, 353–359.

5. Rao, H. S. P.; Jothilingam, S. *J. Org. Chem.* **2004**, *68*, 5392–5394.
6. Singh, S. B. *Indian J. Chem. B* **1981**, *20*, 810.
7. *Representative procedure:* The enedione **1a** (50 mg, 0.13 mmol), formic acid (85%, 0.5 mL) and concd H_2SO_4 (3 mol %) were stirred in a sealed tube (10 mL) under MW irradiation in a mono-mode MW reactor (CEM Discover BenchMate) at 100 °C, 200 W for 2 min until completion of the reaction (TLC). The cooled reaction mixture was diluted with dichloromethane (10 mL), washed with water (2 × 10 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent and column purification over a short column of silica gel (100–200 mesh, 1 cm × 10 cm) using hexanes/ethyl acetate (9:1) as eluent furnished benzil **3a** (52 mg, 96%) whose analytical and spectral data matched those reported.
8. Bikales, N. M.; Becker, E. I. *J. Org. Chem.* **1956**, *21*, 1405–1407.
9. Demirdji, S. H.; Haddadin, M. J.; Issidorides, C. H. *J. Heterocycl. Chem.* **1985**, *22*, 495–496.
10. We thank the referee for suggesting this mechanism.
11. ^{18}O formic acid was prepared by equilibrating formic acid (85%) with $H_2{}^{18}O$ (95%) under a dry N_2 atm at 25 °C for 24 h. The percentage of incorporation of ^{18}O in formic acid was ascertained by MS analysis.
12. Lutz, R. E.; Boykin, D. W. *J. Am. Chem. Soc.* **1967**, *32*, 1179–1183.