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Published

2022

Journal Title

The Journal of Organic Chemistry

Version

Accepted Manuscript (AM)

DOI

[10.1021/acs.joc.2c01020](https://doi.org/10.1021/acs.joc.2c01020)

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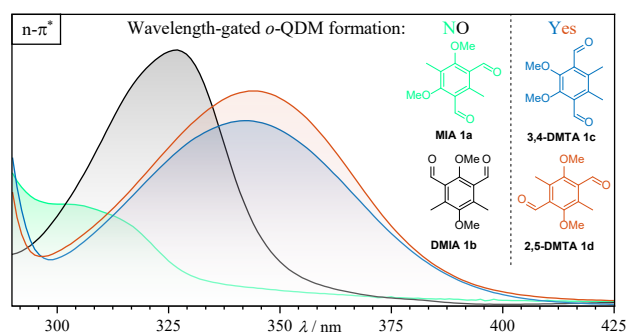
Regioisomerism in Symmetric Dimethyl Dialdehydes Dictates their Photochemical Reactivity

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ABSTRACT: We herein report the first light-driven selective monoderivatization (desymmetrization) of two chemically equivalent carbonyl-groups in a single chromophore. By comparison of four symmetric regioisomers featuring two equivalent *ortho*-methylbenzaldehyde units, we identify dimethylterephthalaldehydes (DMTAs) in which these units can be activated in a dual wavelength-selective fashion. The visible light and UV-light DMTAs undergo two consecutive Diels-Alder reactions exhibiting near quantitative *endo*-selectivity (> 99 %) and provide excellent yields (96-98 %). The influence of the regioisomerism of the dialdehydes on their photochemical behaviour is profound, evidenced by an in-depth investigation of their photochemical performance. We exemplify the capability of the photosystems *via* the synthesis of complex Diels-Alder adducts with various dienophiles, including alkynes.



INTRODUCTION

Photochemically induced, catalyst free processes that proceed rapidly under mild conditions allow for the generation of a diverse range of organic structures.^{1,2} The use of light to gain spatial and temporal control over chemical reactions² finds application in various areas including conjugation of (bio-) macromolecules,³ polymer networks,⁴ photopatterning,⁵ and 3D-printing.⁶⁻⁸ In recent years, exploiting the difference in photon energies at various wavelengths has added an additional level of control over photochemical reactions.^{9,10} Tuning the wavelength of the incident light provides the ability to access the orthogonal reactivity of disparate chromophores.¹¹ The photoenolization/Diels-Alder (PEDA) reaction has been widely employed for applications including, synthesis of natural products,^{12,13,14} complex polyheterocycles,^{15, 16} microparticles,¹⁷ photoligation,¹⁸ sequence-defined polymers,¹⁹ patterned surfaces,²⁰ and many more. The reaction entails the generation of *ortho*-

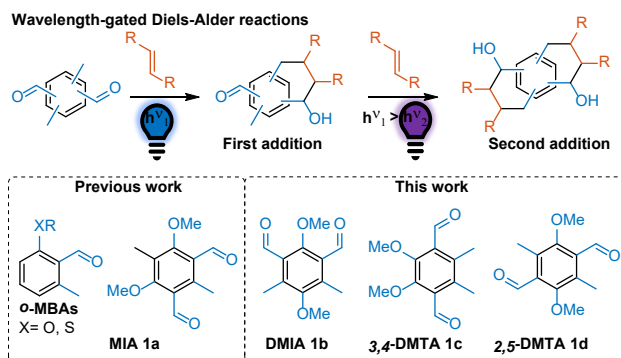
quinodimethanes (*o*-QDMs) *via* enolization of carbonyl compounds, followed by a thermal Diels-Alder reaction.²¹ To the best of our knowledge, the role of isomerism on the absorption profile, reactivity and selectivity of such PEDA systems has not been explored yet.

Molecules that can form two *o*-QDMs from a single aromatic ring were originally introduced by Meador and coworkers.²²⁻²⁵ However, it was only established later that *ortho*-methylbenzaldehydes featuring an electron donating ether or thioether moiety adjacent to the carbonyl group are particularly well-disposed to form reactive *o*-QDMs under irradiation with UV²⁰ or visible²⁶ light.

A recent study by Coote and coworkers theoretically investigated the role of substituents and dienophiles and found that the reaction is tolerant of most substitutions – critically broadening the potential synthetic toolbox.²⁷ PEDA reactions where each enolization system can be accessed with an orthogonal wavelength are fascinating entities, opening the door to modify and implement this efficient reaction into complex molecular structures. Indeed, we recently introduced unsymmetric methylisophthalaldehydes (MIAs), which undergo two wavelength-gated PEDA reactions to form heterobifunctional adducts.²⁸ Therein, we found that the activation in a wavelength-selective fashion is only feasible when two chemically non-equivalent carbonyl-compounds are present in the chromophore.²⁸

In general, the monoderivatization (desymmetrization) of chemically equivalent functional groups represents a formi-

dable challenge and requires well optimized reaction conditions.^{29, 30} For instance, the monoderivatization of 1,*n*-symmetrical diols to monoxan succeeds in a biphasic mixture,³¹ whereas the conversion to monoesters can be achieved by enzymatic reactions.³² To the best of our knowledge, a selective photochemical monoderivatization of two or more chemically equivalent functional groups has not been reported yet.



Scheme 1: (Top) Generalized wavelength-gated Diels-Alder reaction of dimethyldialdehydes. At the longer wavelength, only the first addition of a dienophile occurs whereas at a shorter wavelength the addition of a second equivalent of dienophile occurs. (Bottom left) *o*-MBAs featuring an XR-group serve as high quantum yield substrates for photochemically generated *ortho*-quinodimethanes.³³ Symmetric **MIA 1a** introduced in previous works²⁸ serving as benchmark in this work. (Bottom right) All possible regioisomers containing two *o*-MBA motifs examined in this work.

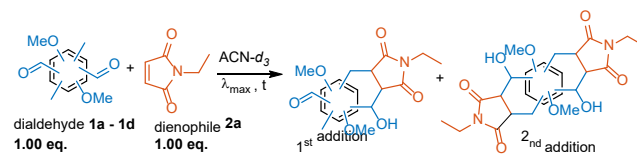
Herein, we establish the photochemical properties of series of symmetric dimethyldialdehydes featuring two chemically equivalent carbonyl groups, relative to the literature known symmetric **MIA 1a** (refer to Scheme 1). We find that the molecular regioisomerism has a critical effect on the absorptivity and reactivity. More specifically, we provide a general approach to alter the substitution pattern of a specific class of symmetric chromophores that can be exploited to tailor their photochemical reactivity.

RESULTS AND DISCUSSION

To this end, three unknown dialdehydes, i.e., dimethylisophthalaldehyde (**DMIA 1b**), 3,4-dimethylterephthalaldehyde (**3,4-DMTA 1c**) and 2,5-dimethylterephthalaldehyde (**3,4-DMTA 1d**) (Scheme 1), are explored. In these symmetric molecules, two *ortho*-methylbenzaldehydes motifs are combined in all possible symmetries, without a methyl group forming a bridgehead atom. All dialdehydes **1a** – **1d** were obtained in a similar fashion *via* the formylation of the respective dimethyl-resorcinols, -catechols and -hydroquinones using a modified literature procedure³⁴ and subsequent methylation of the OH-groups (refer to Section 3, SI). The synthetic procedure represents a substantial improvement in yield and simplicity compared to our previous reports.²⁸ The dialdehydes vary significantly in their absorption spectra (refer to Fig. S30, SI), suggesting that their photochemical behaviour also differs. In our previous work, a thorough investigation of unsymmetric MIAs

using monochromatic laser-light revealed that the reaction quantum yield involving the first *ortho*-formyl group was significantly higher than for the second *para*-formyl group. We therefore hypothesized that the missing electron donating ether group adjacent to the *para*-formyl group plays an important role for the reduced quantum yield consequentially enabelling the wavelength-gated addition. Since the abstraction of both protons in the excited state occurs on the methyl-group for the MIAs, further investigation into the cause of the wavelength-selective fashion of the reaction could not be carried out. To identify which dialdehydes are capable of the aforementioned wavelength-gated generation of two equivalents of *o*-QDMs, photoreaction experiments in the presence of the dienophile **2a** were carried out on the NMR-scale under stoichiometric conditions in acetonitrile. In principle, the results of such an experiment falls between two extreme cases: In a perfectly wavelength-selective, step-wise reaction and at full conversion of the dienophile, solely the 1st addition product will be observed. At the opposite extreme, when the 2nd addition occurs at a infinitely higher reaction quantum yield, a 1:1 mixture of the educt dialdehyde and the 2nd adduct will be observed. The results of these experiments are summarized in Table 1.

Table 1: Wavelength-dependent Photochemical Selectivity in ACN



Photochemical selectivity of the photoinduced cycloaddition of dialdehydes **1a** – **1d** with dienophile **2a** under stoichiometric conditions at different wavelengths. The irradiation time was chosen to achieve full conversion of the dienophile. The conversion was determined *via* ¹H-NMR spectroscopy using, 1,4-dimethoxybenzene as an internal standard.

Dialdehyde	λ_{max} [nm]	P_{LED} [W]	t [min]	X 1st [%]	1st : 2nd [%]
MIA 1a	415	20	1440	37	55:45
MIA 1a	385	12	15	38	50:50
MIA 1a	365	12.5	5	35	51:49
DMIA 1b	415	20	--	--	--
DMIA 1b	385	12	30	2	12:88
DMIA 1b	365	12.5	25	<1	7:93
3,4-DMTA 1c	415	10	10	84	84:16
3,4-DMTA 1c	385	12	5	44	75:25
3,4-DMTA 1c	365	12.5	5	23	50:50
2,5-DMTA 1d	415	10	40	59	82:18
2,5-DMTA 1d	385	12	5	35	46:54
2,5-DMTA 1d	365	12.5	5	25	60:40

The experimental details are described in the Supporting Information section 4.a-d.

MIA **1a** was found to react very slowly under LED irradiation centred at 415 nm, which is expected due to very low extinction coefficients at these wavelengths (refer to Fig. S1 and S30 SI). At all three wavelengths 415 nm, 385 nm and 365 nm, the selectivity for the 1st addition is low, consistent with our earlier reports.²⁸

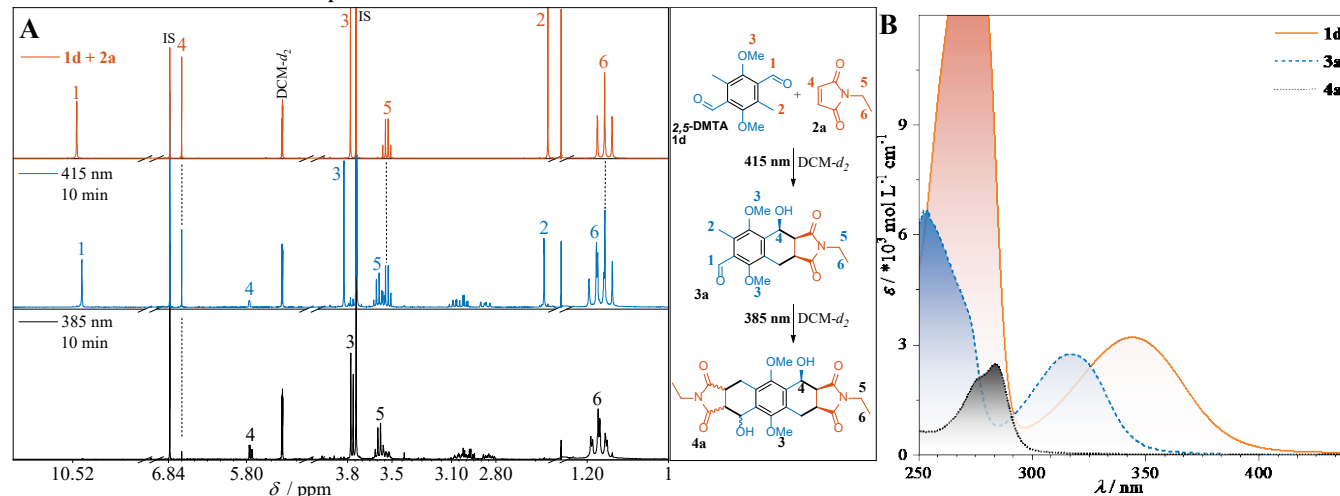


Figure 1. A) (Top) Reaction mixture of 1.00 eq **1d** (10 mmol L⁻¹), 2.19 eq **2a** and internal standard (IS, 1,4-dimethoxybenzene) in DCM-*d*₂ before irradiation (middle) after irradiation with a 415 nm LED (10 W) for 10 min (bottom) and after irradiation with a 385 nm LED (12 W) for 10 min. Marked are key resonances of educts **1d**, **2a** and products **3a** and **4a** (B) UV-VIS absorption of isolated samples of **1d**, 1st adduct **3a**, 2nd adduct **4a** recorded in acetonitrile evidencing the hypsochromic shift of the Diels-Alder products.

To further improve the selectivity of the wavelength-gated step-wise Diels-Alder reaction, we investigated the influence of the solvent for **1a** (refer to Fig. S13 – 19) compared to **1d** (refer to Fig. S21 – 28). While **1a** shows very good performance in different solvents, the selectivity remains low. On the other hand, the selectivity of **1d** substantially increased in acetone and DCM. In Fig. 1a, such a reaction is

DMIA **1b** does not react under irradiation with 415 nm. Under irradiation with shorter wavelengths, the 2nd adduct was primarily formed, combined with various side products. Finally, 3,4-DMTA **1c** and 2,5-DMTA **1d** exhibited medium to good selectivity for the 1st addition at 415 nm with only minor 2nd adduct formation detected. As expected, increasing amounts of the 2nd adduct were observed at shorter wavelengths.

shown, using an excess of dienophile. By irradiation with 415 nm, the mono-adduct **3a** is primarily formed. By consecutive reduction of the irradiation wavelength to 385 nm the 2nd adduct **4a** could be obtained. The absorption spectra of isolated **1d**, **3a** and **4a** show a hypsochromic shift caused by the conversion of the carbonyl groups.

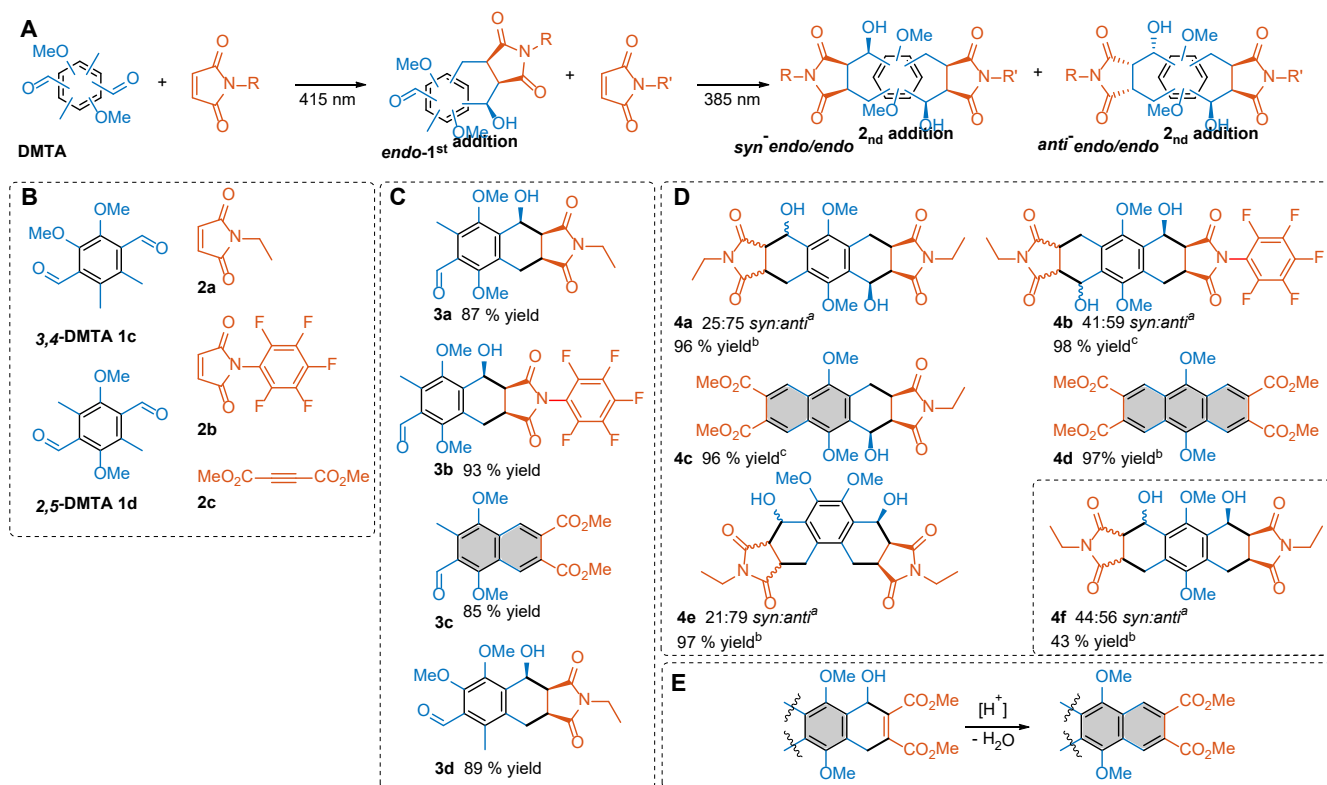


Figure 2. (A) Generalized wavelength-gated Diels-Alder reaction of DMTAs **1c** and **1d** with dienophiles **2a** – **2c**. At 415 nm, the 1st addition forming an *endo*-adduct is observed. At 385 nm, the 2nd addition leads to two diastereomeric products *via syn-endo* or *anti-endo* addition. (B) Substrates for the preparative synthesis of first addition products (C) and second addition products (D). Symmetric products **4a**, **4d**, **4e** and **4f** are obtained (E) shows the rapid, acid catalysed E1-elimination introduced in our earlier work³⁵ that leads to naphthalenes **3c** and **4c** as well as anthracene **4d**, which is carried out after the photoinduced Diels-Alder cycloaddition by the addition of *para*-toluenesulfonic acid. ^a Determined by LCMS; ^b Combined yield for 1st and 2nd addition; ^c Isolated yield for the 2nd addition.

During the reaction of dialdehyde (chromophore A) to the 1st adduct (chromophore B), typically a mixture of chromophores A and B is initially being formed. In such a mixture, the wavelength-dependent reactivity of the components, and therefore the selectivity of competing reactions, are difficult to predict.³⁶ In the herein presented case, the shift of the absorptivity of the 1st adduct **3a** (compared to **1d**) provides control over the reaction by choice of wavelength. Similar behaviour was observed for **1c** and **3d** (refer to Fig. S36). To summarise, stepwise conversion of two equivalents of carbonyl groups can be controlled in a wavelength-gated manner for dialdehydes **1c** and **1d**, whereas **1a** and **1b** do not allow for such a level of control.

In the following step, we explored the synthetic breadth of the wavelength-gated photoreactions and investigated the diastereoselectivity of both reactions (Fig. 2). First, we obtained the mono-adducts **3a** – **3d** in good yields, using a slight excess (1.10 eq.) of dienophiles **2a-2c** and performing the reaction in DCM (for details, refer to Section 5, SI). Notably, naphthalene **3c** was obtained after irradiation and consecutive quantitative E1-elimination at ambient temperature. Conversion of the residual carbonyl group of **3c** during irradiation with various wavelengths was not observed. For adducts **3a**, **3b** and **3d**, solely the *endo*-adducts were formed. Increasing the equivalents of

dienophile and irradiation with 385 nm lead to homobifunctional adducts **4a** and **4e** as diastereomeric mixtures of two meso-compounds. Here, the *o*-QDM intermediate generated during the 1st addition can either be attacked by the dienophiles in *syn* or *anti*-trajectory forming the two possible cycloadducts. Surprisingly, we observed for both substrates a tendency to form the *anti*-product, despite the spatial separation between the reaction centres. The 2nd addition furthermore shows a high *endo*-selectivity, similar to the 1st addition. For further discussion on the diastereoselectivity and the relevant symmetry elements of the formed cycloadducts refer to the supporting information section 7. A two-fold addition of alkyne **2c** and subsequent acid gated E1-elimination provided anthracene **4d**. It is worthy to note that **4d** is photosensitive and its absorption maximum is shifted to $\lambda_{\text{max}} = 410\text{ nm}$, evidencing the advantage of the temporal control over the cycloaddition and the following aromatization.³⁵ The isolated 1st adduct **3b** was converted to the heterobifunctional 2nd adduct **4b** in high yields. Furthermore, **3a** was successfully converted to **4c** featuring an uncommon tetrahydroanthracenol scaffold. We chose electron-deficient maleimides **2a** and **2b** based on their ability to form a single diastereomer for the 1st addition and two diastereomers for the 2nd addition and electron-deficient alkynes. If non-cyclic dienophiles such as

fumerates were used would be obtained. For the alkyne, diastereoisomerism does not play a role since the E1-eliminated products do not feature stereocenters.

CONCLUSIONS

In conclusion, we establish that symmetric dialdehydes, featuring two *ortho*-methylbenzaldehyde units, vary significantly in absorptivity and wavelength-dependent photochemical reactivity. Dimethyl-terephthalaldehydes **1c** and **1d** are activated in a wavelength-gated fashion allowing for the assembly of complex, linear scaffolds. To the best of our knowledge, the influence of the isomerism on the photochemical behaviour of *o*-QDM forming carbonyl-compounds has not been systematically studied, both in theoretical and experimental works. The herein presented methodology represents the first selective monoderivatization (desymmetrization) of two chemically equivalent moieties in a single chromophore. The methodology therefore represents a considerable advance that might be transferred to other known photoreactive chromophore systems.

ASSOCIATED CONTENT

Supporting Information

Materials, instrumentation, synthetic procedures, photoreactions, copies of UV-vis, fluorescence and NMR spectra and LCMS results. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

C.B.-K. is grateful for support by the Deutsche Forschungsgemeinschaft (DFG) under Germany's Excellence Strategy via the Excellence Cluster "3D Matter Made to Order" (Grant No. EXC-2082/1-390761711). C. B.-K. acknowledges funding from the Australian Research Council (ARC) in the form of a Laureate Fellowship (FL170100014) enabling his photochemical research pro-gram as well as continued key support from the Queensland University of Technology (QUT). Prof. Martin Wegner (KIT) is thanked for his continuous support and active contribution to our photochemistry research program.

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