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PHOTOCHEMICAL RING CLOSURE OF MUCONIC ACID ANHYDRIDE

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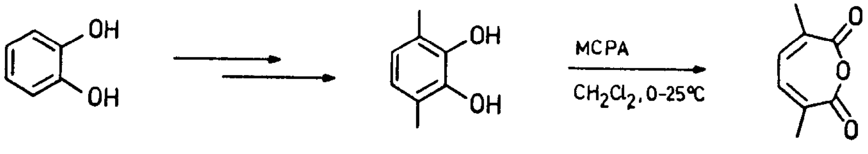
Summary: 2.5-Dimethyl muconic acid anhydride has been synthesized in three steps from catechol and transformed via a high yielding photochemical ring closure into cis-1,5-dimethyl-3-azabicyclo [3.2.0] heptane-2,4-dione.

Functionalized derivatives of cycloheptadienes or heterocyclic derivatives thereof have been known for a long time to ring close photochemically [1]. In most cases the yield of these reactions is not very good. Belluš and coworkers have recently reported a synthesis of cis-N-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo [3.2.0] heptane-2,4-dione 4, which is highly active against Botrytis cinerea, a gray mould fungus on grapes [2]. This synthesis relied on the photochemical [2 + 2] cycloaddition between ethylene and dimethylmaleic acid anhydride which proceeded unfortunately only below -50° C [3].

The synthesis of 2,5-dimethylmuconic acid anhydride 1 could easily be achieved in 80 % yield by treating 2,5-dimethylcatechol [4] with a slight excess of MCPA at room temperature [6] (scheme I). The product could be separated from the meta-chlorobenzoic acid by low temperature filtration at -78° C.



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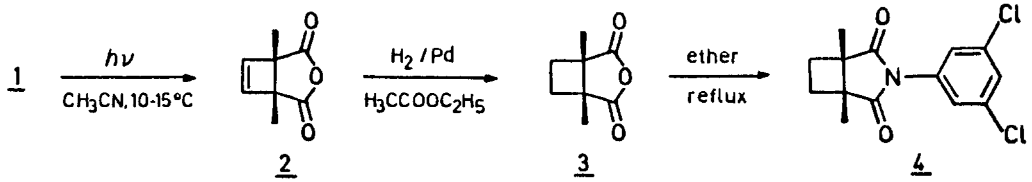
Scheme I

A 0.12 molar solution of muconic acid anhydride in acetonitrile was smoothly transformed in high yield by irradiation at room temperature with a pyrex filter into cis-2,5-dimethyl-3-oxabicyclo [3.2.0] heptane-2,4-dione (scheme II). This product was directly reduced and the isolated yield over the two steps was 86 %. The anhydride could be treated with 3,5-dichloroaniline to yield the desired product [2]. The imide is now available in three high yielding steps starting from 2,5-dimethyl muconic acid anhydride in 58 % overall yield. The sequence of photochemical ring closure, reduction, imide formation is not restricted to the dimethyl derivative, but has also been achieved starting from 3-t-butylmuconic acid anhydride [7,8]. There are several advantages of this sequence to be mentioned:



Scheme II

1. The use of muconic acid anhydride as starting material allows to alter easily substituents using different starting materials.
2. The photochemical ring closure avoids the problems of crossed addition [2].
3. The chromophores of the starting material ($\lambda_{max.}$ = 286 nm) and the product ($\lambda_{max.}$ < 200 nm) make it possible to irradiate the starting material selectively, thereby ensuring a high yield of the photochemical transformation.

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References and Notes:

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[5] All new compounds gave satisfactory spectroscopic data.

[6] 2,5-dimethylmuconic acid anhydride: ^{1}H-NMR (90 MHz in CDH_3): 6.47 (s, 2H); 2.15 (s, 6H). ^{13}C-NMR (90,5 MHz in $CHCl_3$): 161.0 (s); 133.6 (s); 131.7 (d); 21.2 (q). IR (in $CHCl_3$): 3030w, 1770sh, 1725s. MS: $M^+_{exp.}$ = 152.0472, $M^+_{theor.}$ = 152.0473.

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[8] 6-t-butyl-3-oxabicyclo [3.2.0] hept-6-ene-2,4-dione: ^{1}H-NMR (90 MHz in $CDCl_3$): 6.00 (s, 1H); 3.95 (d, J = 3Hz, 1H); 3.77 (d, J = 3Hz, 1H); 1.12 (s, 4H). 6-t-butyl-3-oxabicyclo [3.2.0] heptane-2,4-dione: ^{1}H-NMR (360 MHz in $CDCl_3$): 3.53 (d x d, br, $J_{5,6}$ = 10.1 Hz, $J_{1,5}$ = 6.8 Hz, 1H); 3.43 (d x d x d, $J_{1,5}$ = 6.8 Hz, $J_{1,7}$ = 6.1 Hz, $J_{1,7}$ = 10.0 Hz, 1H); 2.88 (d x d x d, $J_{5.6}$ = 10 Hz, $J_{5,2}$ = 10 Hz, $J_{5,7}$ = 10 Hz, 1H); 2.65 (d x d x d x d, $J_{1,7'}$ = 10 Hz, $J_{5,7'}$ = 1.5 Hz, $J_{6,7'}$ = 10 Hz, $J_{7,7'}$ = 12.9 Hz, 1H); 2.28 (d x d x d x d, $J_{1,7}$ = 6.1 Hz, $J_{5,7}$ = 0.5 Hz, $J_{6,7}$ = 10 Hz, $J_{7,7}$ = 12.9 Hz, 1H).

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