

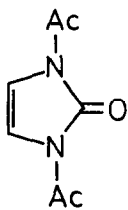
CYCLOADDITION REACTIONS OF 1,3-DIACETYLMIDAZOLIN-2-ONE

Ralph A. Whitney

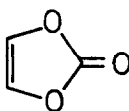
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Abstract: 1,3-Diacetylimidazolin-2-one, for which a new preparation is described, has been found to undergo thermal cycloaddition reactions with a limited number of dienes; in contrast it undergoes photochemical cycloadditions quite readily.

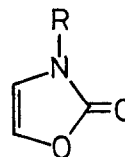
Our interest in the synthesis of natural products containing a cyclic ureido moiety has led us to examine the reactivity of 1,3-diacetylimidazolin-2-one (1)¹ in [4+2] and [2+2] cycloaddition reactions. Similar studies have been reported for vinylene carbonate (2)² and for 4-oxazolin-2-ones (3)³. While the preparation of 1 has been described¹ in the literature we have found it more convenient⁴ to prepare the compound by reduction of hydantoin with diisobutylaluminum hydride (DIBALH) to imidazolin-2-one followed by acetylation as described below.




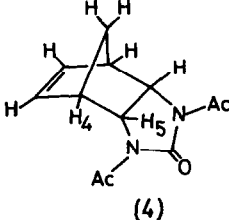
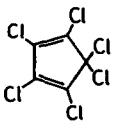
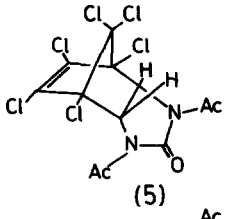
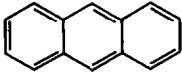
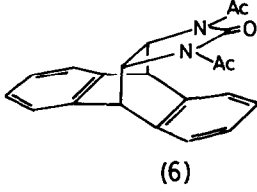

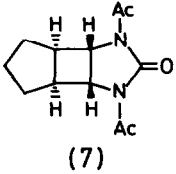

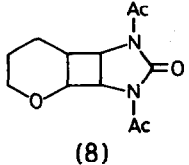
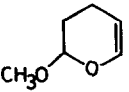
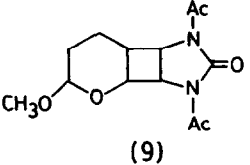
(1)



(2)



(3) R=H, Ac

<u>Diene</u>	<u>Adduct</u> ¹⁰	<u>mp</u>	<u>Yield</u>
		119-20°	69%
		171-2°	68%
		209-10°	78%
<u>Olefin</u>	<u>Adduct</u> ¹⁰	<u>mp</u>	<u>Yield</u>
		143-4°	30%
		mixture of diastereomers	93%
		mixture of diastereomers	79%

The results of the Diels-Alder reactions of 1 are listed in the Table. All reactions were conducted with xylene as solvent in a sealed tube at 180°; an excess of diene was employed. The stereochemistry of the cyclopentadiene adduct (4) was assigned on the basis of proton coupling constants⁵, J_{H_4, H_5} being 2 Hz. In addition to the cycloadducts indicated, 1,3-diacetylimidazolin-2-one failed to react with 1,3-nonadiene (xylene, 180°) and with 3,6-di(2-pyridyl)-1,2,4,5-tetrazine⁶ (ethyl acetate, 78°) in an inverse electron demand⁷ Diels-Alder reaction. These results indicate a greater reluctance by 1 to participate in [4+2] cycloaddition reactions than either vinylene carbonate² or 4-oxazolin-2-ones³. This lowered reactivity can be associated with the imide functional group attached to the olefinic bond; a similar result has been observed in the decreased reactivity of enimides with electrophilic reagents⁸. In addition 1 failed to react with dichloroketene.

Not surprisingly⁹ the photochemistry of 1 had proved to be quite useful as shown by the results in the Table. Photolyses were performed at room temperature under a nitrogen atmosphere with a 450 W Hanovia lamp filtered with Corex. Acetone (275 ml) was used as solvent and sensitizer with an excess of olefin (5-10 ml per g of 1) present. The cyclopentene adduct (7) was isolated by Kugelrohr distillation (130°, 1 Torr) followed by recrystallization and the anti stereochemistry was assigned on the basis of a small coupling (<1 Hz) between the bridgehead protons. The use of enol ethers in the photolysis gave good yields of cycloadducts with dihydropyran giving a mixture of two diastereomeric products and 2-methoxy-3,4-dihydropyran giving four diastereomeric products that were not readily separable by chromatography. Further application of this photochemical reaction to the synthesis of nature products will be reported presently.

Experimental

Hydantoin (2.0g, 20 mmole) was suspended with stirring in dry THF (20 ml) cooled to 0° under a nitrogen atmosphere. DIBALH (35 ml, 25% in toluene) was added dropwise with stirring over 30 minutes with stirring continued for an additional hour at 0°. Careful addition of 90% aq. methanol (150 ml), refluxing overnight, filtration and evaporation to dryness gave imidazolin-2-one (1.4g) which was acetylated with acetic anhydride (10 ml) and trifluoroacetic acid (0.5 ml) at reflux for 6 h. Evaporation to dryness, dissolution in ether: CH₂Cl₂ (10:1), filtration and evaporation to dryness gave 1,3-diacetylimidazolin-2-one (1.9g, 56%) as a white solid mp 105° on recrystallization from ether (lit.¹ 106°).

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