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Dipolar cycloaddition of carbonyl ylides to *para*-quinoneimides: a facile route to bicyclo[3.2.1] and [2.2.1] systems[†]

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Abstract—Five- and six-membered carbonyl ylides formed from rhodium carbenoids add to *p*-quininoneimides to afford bicyclic compounds in good yields. © 2001 Elsevier Science Ltd. All rights reserved.

Benzoquinones are a very important class of organic compounds, their chemistry being exploited for the synthesis of a variety of natural and unnatural compounds of value.[1] Surprisingly, their aza analogues, despite having a long history in chemistry,[2,3] have attracted only limited attention. The scant information available on *p*-quinoneimides is concerned mainly with the addition of nucleophiles;[4] very little work involving the cycloaddition of *p*-quinoneimides has been reported.[3] One area that remains totally unexplored is their reactivity towards various dipoles.[5] Against this literature backdrop and in the context of our general interest in the cycloadditions of quinones and related species,[6,7] we initiated some studies on the addition of carbonyl ylide dipoles to *p*-quinoneimides. Earlier our group[8] and, very recently, Pirrung et al.[9] have studied the reactivity of carbonyl ylides towards *o*- and *p*-quinones, respectively. It is noteworthy that tandem cyclization–cycloaddition reactions of rhodium carbenoids have emerged as a powerful tool for heterocyclic construction, thanks mainly to the extensive work by Padwa.[10,11] Our preliminary results are delineated here.

In an initial experiment, the quinoneimide **1a** was treated with the diazo compound **2a** in benzene under Rh(II) catalysis. The carbonyl ylide formed in situ adds to the endocyclic double bond of the quinoneimide yielding the bicyclo[2.2.1] adduct **3a** (Scheme 1).[12]

The structure of the adduct was established by spectroscopic methods. The regiochemistry as well as the stereochemistry was confirmed by NOE analysis (Fig. 1).[‡]

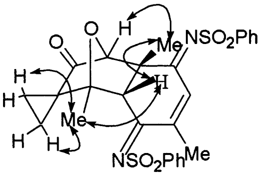
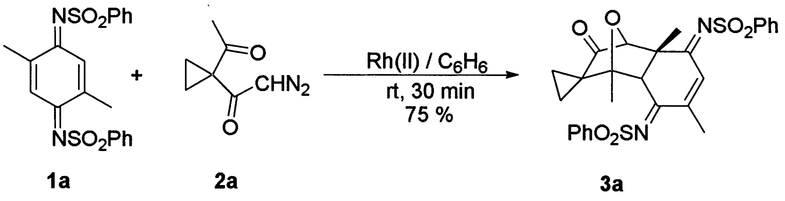


Figure 1. Selected NOE data for **3a**.



Scheme 1.

Keywords: dipolar cycloaddition; quinoneimide; carbonyl ylide.

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[†] Dedicated with best wishes to Professor Koji Nakanishi on the occasion of his 75th birthday.

[‡] Typical experimental procedure and data for **3a**: The $Rh_2(OAc)_4$ catalyzed reaction of the carbonyl ylide precursor **2a** (36 mg, 0.236 mmol) and the quinoneimide **1a** (56 mg, 0.135 mmol) in 2 mL anhydrous benzene at room temperature for 30 min afforded the adduct **3a** (58 mg, 75 %). ^{1}H NMR (500 MHz): δ 7.95–7.98(m, 5H), 7.55–7.67(m, 6H), 4.43(s, 1H), 4.39(s, 1H), 2.18(d, $J=1$ Hz, 3H), 1.50(ddd, $J=9.7$, 7.6 and 4.1 Hz, 1H), 1.43(ddd, $J=9.7$, 6.6 and 4.1 Hz, 1H), 1.32(ddd, $J=9.8$, 6.6 and 4.1 Hz, 1H), 1.15(ddd, $J=9.8$, 7.6 and 4 Hz, 1H), 1.38(s, 3H), 1.28(s, 3H). ^{13}C NMR (75 MHz): 208.69, 176.86, 176.47, 151.92, 140.80, 140.64, 133.81, 133.36, 133.16, 129.09, 129.03, 127.15, 90.11, 89.94, 58.92, 54.12, 42.48, 21.43, 19.35, 15.57, 15.42, 12.73.

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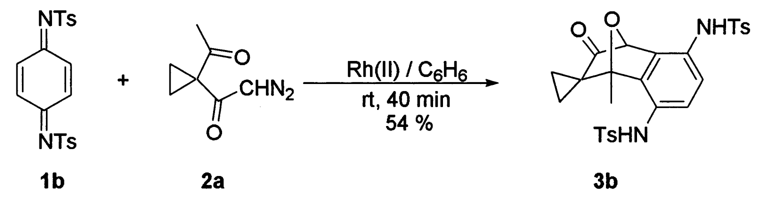
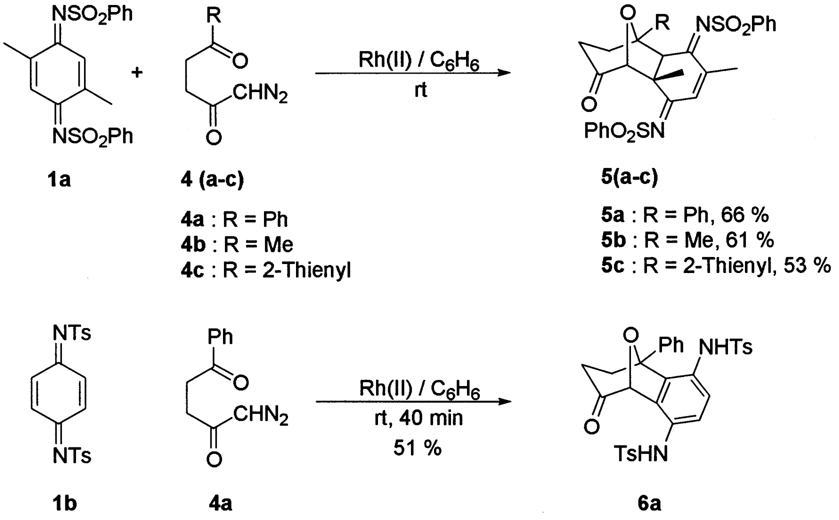


Scheme 2.



Scheme 3.

When the quinoneimide **1b** was employed in the reaction, the initially formed adduct underwent tautomerization to afford **3b** (Scheme 2).

Parallel investigations were carried out with six-membered carbonyl ylides and the results are summarized in Scheme 3.

In conclusion, we have established that carbonyl ylides generated by the cyclization of rhodium carbenoids add to *p*-quinoneimides affording very interesting bicyclic compounds, which are potentially amenable to a number of synthetic transformations. Further work is in progress.

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