Pergamon

Tetrahedron Letters, Vol. 37, No. 20, pp. 3487-3488, 1996

0040-4039/96 $15.00 + 0.00

S0040-4039(96)00641-7

Transfer of the R^{1}C-N(*t*Boc)-CR^2 Unit from 2,4-Dihydropyrrolo[3,4-*b*]indoles to Dienophiles by Diels-Alder and Retro-Diels-Alder Reactions

Chin-Kang Sha,* Jenn-Feng Yang and Chin-Jung Chang

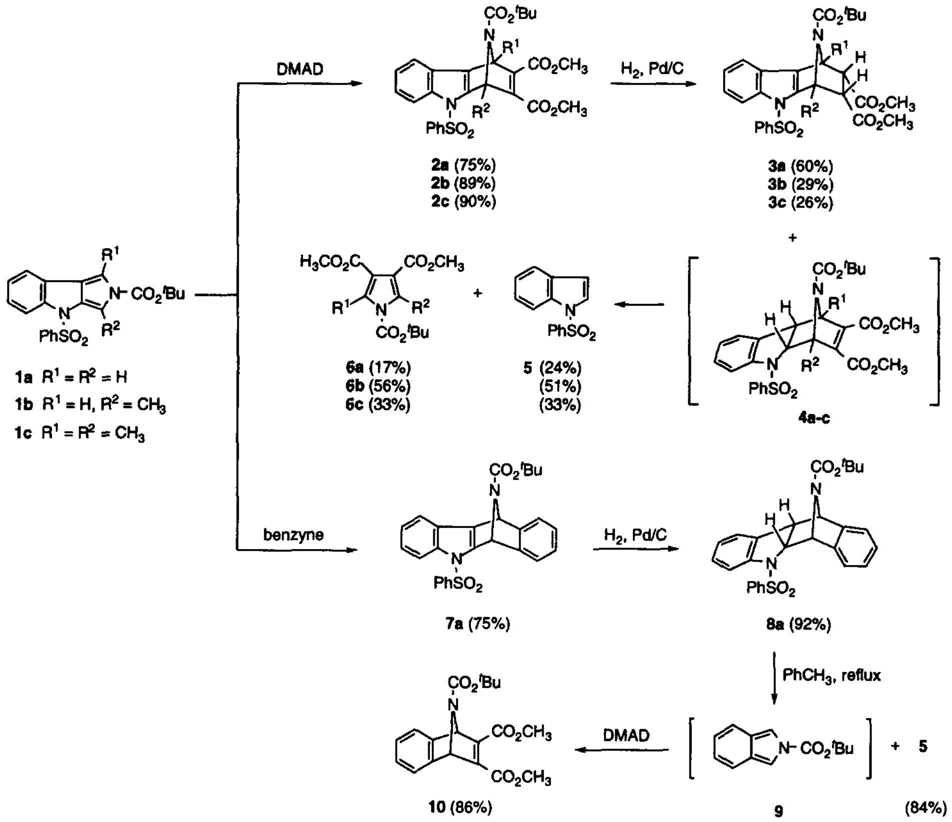
Department of Chemistry, National Tsing Hua University
Hsinchu 300, Taiwan, R.O.C.

Abstract: Hydrogenation of Diels-Alder Adducts **2a-c** and **7a** of 2,4-dihydropyrrolo[3,4-*b*]indoles **1a-c** and DMAD or benzyne induced retro-Diels-Alder reactions to give indole **5** and pyrroles **6a-c** or isoindole **9**.

In our previous study we had reported the efficient synthesis of 2,4-dihydropyrrolo[3,4-*b*]indole ring systems **1**, and their facile Diels-Alder reactions with reactive dienophiles.[1] This cycloaddition reaction of 2,4-dihydropyrrolo[3,4-*b*]indole was later applied to the total synthesis of anticancer alkaloid ellipticine.[2] In this letter, we describe the interesting Diels-Alder and retro-Diels-Alder reactions of 2,4-dihydropyrrolo[3,4-*b*]indole,[3] which effect the transfer of R^{1}C-N(*t*Boc)-CR^2 unit[4] from 2,4-dihydropyrrolo[3,4-*b*]indoles to dienophiles.

Diels-Alder reaction of **1a-c** with dimethyl acetylenedicarboxylate (DMAD) gave cycloadducts **2a-c** in good to excellent yields (75-90%). Hydrogenation of **2a-c** using 10% Pd on carbon as catalyst afforded compounds **3a-c** and retro-Diels-Alder products **5** and **6a-c**. Apparently hydrogenation **2a-c** occurred not only at the electron-deficient double bond but also at the indole portion to give **3a-c** and **4a-c**. Indolines **4a-c** immediately underwent retro-Diels-Alder reactions to give indole **5** and pyrrole derivatives **6a-c**. In order to make hydrogenation to occur specifically at the indole double bond, benzyne was used as the dienophile. Thus, Diels-Alder reaction of **1a** with benzyne, generated from benzenediazonium-2-carboxylate, gave cycloadduct **7a** (75%). Hydrogenation of **7a** with 10% Pd on carbon as catalyst yielded a stable compound **8a** (92%). Heating **8a** in refluxing toluene in the presence of DMAD produced indole **5** (84%) and cycloadduct **10** (86%).

In conclusion, we have demonstrated the transfer of the R^{1}C-N(*t*Boc)-CR^2 unit of 2,4-dihydropyrrolo[3,4-*b*]indole to dienophiles, such as DMAD and benzyne, by Diels-Alder



and retro-Diels-Alder reaction. It is important to note that the indole double bond in the bridged bicyclic systems **2a-c** and **7a** can be hydrogenated readily. We also found that compound **8a**, the formal cycloadduct of indole and isoindole, is unusually stable at room temperature. Other closely related Diels-Alder and retro-Diels-Alder reaction sequences are currently under investigation in our laboratory.

Acknowledgment. This work is supported by a grant from the National Science Council of the Republic of China (NSC-85-2113-M007-016).

References:

1. Sha, C.-K.; Chuang, K.-S.; Young, J.-J. *J. Chem. Soc., Chem. Commun.* **1984**, 1552. Sha, C.-K.; Chuang, K.-S.; Wey, S.-J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 977.
2. Sha, C.-K.; Yang, J.-F. *Tetrahedron* **1992**, *48*, 10645.
3. For a review on Diels-Alder and retro-Diels-Alder reaction see: Ho, T.-L. *Tandem Organic Reactions*; Wiley: New York, 1992; pp231.
4. For the chemistry of the closely related azomethine ylide unit see: Alanine, A. I. D.; Fishwick, C. W. G.; *Tetrahedron Lett.* **1989**, *30*, 4443. Grigg, R.; Heaney, F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 198; and references cited therein.

(*Received in China* 11 *December* 1995; *accepted* 25 *March* 1996)