Pergamon

SCIENCE DIRECT

Tetrahedron Letters 44 (2003) 4339–4342

TETRAHEDRON
LETTERS

Surprising 1,7-cyclization of vinyl carbonyl ylides generated from reaction of indanetrione with vinyl diazo compounds

Masashi Hamaguchi,[a,*] Kazuma Takahashi,[a] Takumi Oshima[a] and Hatsue Tamura[b,*]

[a] *Department of Materials Chemistry, Graduate School of Engineering, Osaka University, Toyonaka 560-0043, Japan*
[b] *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Toyonaka 560-0043, Japan*

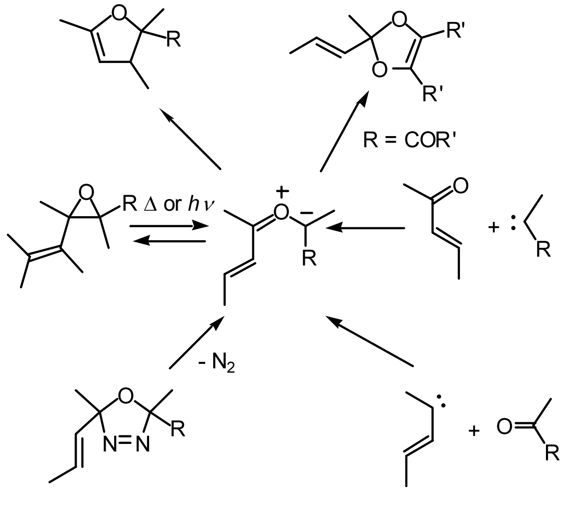
Received 12 March 2003; revised 9 April 2003; accepted 11 April 2003

Abstract—Reactions of tricarbonyl compounds with vinyl diazo compounds **2** were carried out. Reaction of 1,2,3-indanetrione with **2a**,**b**,**c** gave the spiroindan-1,3-dione-2,2′-benzodihydrooxepin **7a**,**b**,**c**, but not normal products oxirane and dihydrofuran derivatives expected from intermediate vinyl carbonyl ylides **4**. Formation of **7** requires isomerization of vinyl carbonyl ylides **4** bearing a (*Z*)-cyanostyryl group to unstable (*E*)-form **5** and subsequent cyclization to oxepin **6** followed by a 1,5-hydrogen shift. However, reaction of **2** with six-membered cyclic tricarbonyl compounds 1,2,3-trioxo-2,3-dihydrophenalene **11** and dimethylalloxane **13** gave the dioxole **12** and the dihydrofuran **14**, respectively, typical products expected from vinyl carbonyl ylides. © 2003 Elsevier Science Ltd. All rights reserved.

The formation and reaction of carbonyl ylides continue to be subject of considerable interest and intensive investigation.[1] The thermal or photochemical ring opening of oxiranes[2] or Δ^3-1,3,4-oxadiazoline[3] and addition of a carbene/carbenoid onto the oxygen atom of a carbonyl group[4] have been known as traditional methods of generation of carbonyl ylides. In spite of enormous studies of carbonyl ylides, studies on vinyl carbonyl ylides via thermal ring opening of vinyloxiranes[5] and the carbenoid–carbonyl reaction[6] are limited (Scheme 1). The thermal ring opening of oxiranes to carbonyl ylides requires high temperature, whereas the generation of carbonyl ylides via the carbenoid–carbonyl reaction can be performed under very mild conditions.

Electron-deficient carbonyl compounds have also been known to react with diazo compounds under mild conditions to give Δ^3-1,3,4-oxadiazoline followed by extrusion of nitrogen to furnish carbonyl ylides.[7] Most of the thus generated carbonyl ylides have been reported to cyclize to dioxoles and also oxiranes as 4π electronic components.[1] It is well-known that diphenyldiazomethane reacts with cyclic tricarbonyl compounds indanetrione **1** and 1,2,3-trioxo-2,3-dihydrophenalene **11** to give an oxirane[8] and a dioxole, [9] respectively. We would like to report the first example of generation of vinyl carbonyl ylides via extrusion of nitrogen from Δ^3-1,3,4-oxadiazoline formed by the 1,3-dipolar cycloaddition reaction of tricarbonyl compounds with vinyl diazo compounds **2** and abnormal 1,7-cyclization of the vinyl carbonyl ylides formed in the reaction of indanetrione **1** with **2**.

A solution of indanetrione **1** (2.00 mmol) and 2-(*p*-chlorophenyl)-4-diazo-4-phenyl-*cis*-2-butenenitrile **2a**



Scheme 1.

Keywords: 1,7-cyclization; 1,5-cyclization; vinyl carbonyl ylides; diazo compounds; indanetrione; benzodihydrooxepins; tricarbonyl compounds.

* Corresponding author. Fax: +81-6-6850-5785; e-mail: hamaro@ch.wani.osaka-u.ac.jp

0040-4039/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0040-4039(03)00936-5

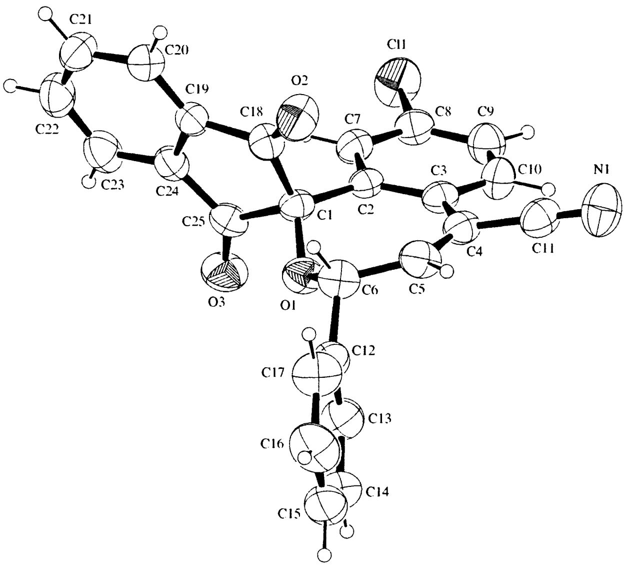
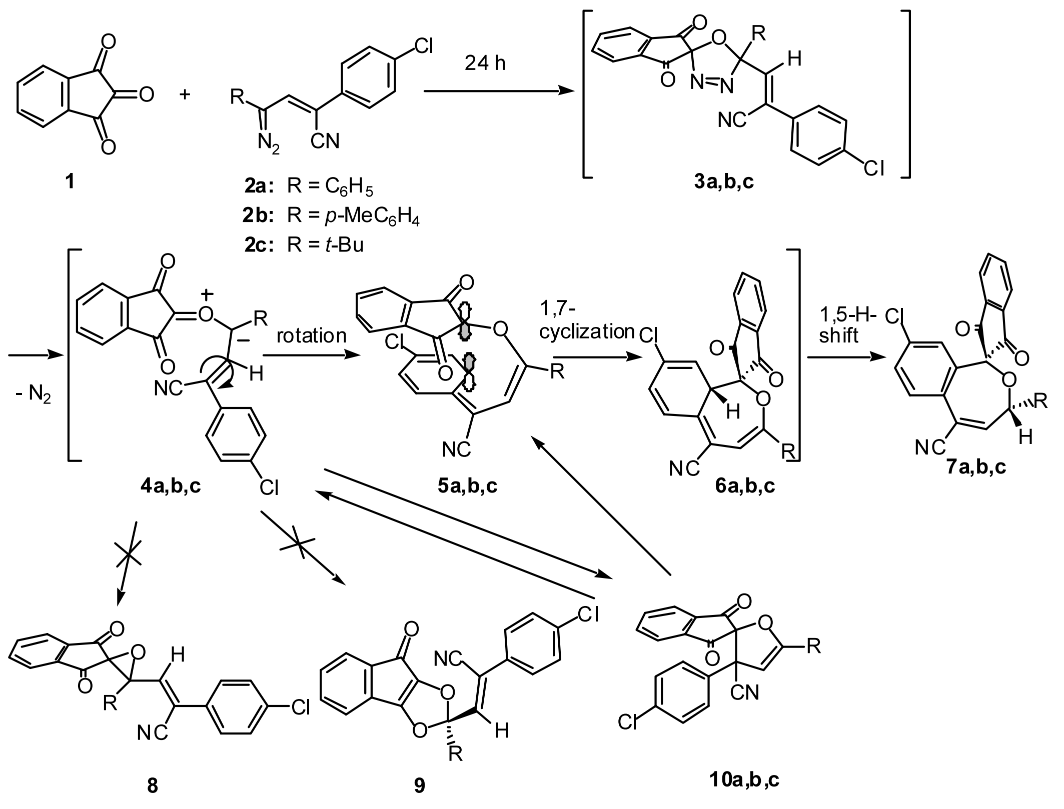


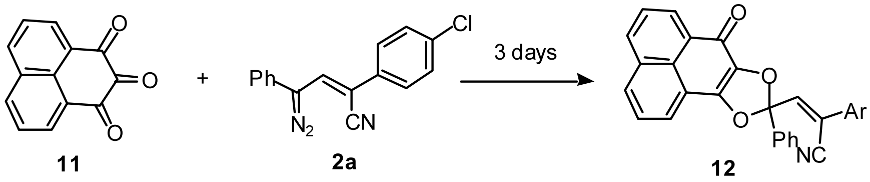
Figure 1. ORTEP view of **7a**.

(2.00 mmol) in 20 ml of CH_2Cl_2 was strirred under an argon atmosphere at room temperature for 24 h. After filtration, the reaction mixure was chromatographed over silica gel to give spiroindan-1,3-dione-2,2′-benzodihydrooxepin **7a** in 77% yield. The ^1H NMR spectrum of three protons of *p*-chlorophenyl group of **7a** showed δ 7.90 (d, $J=8.6$ Hz), 7.44 (dd, $J=2.0$, 8.6 Hz), and 6.87 (d, $J=2.0$ Hz), indicating that one proton of the *p*-chlorophenyl group is replaced by another group. The structure of **7a** was confirmed by X-ray analysis, as shown in Figure 1.[10] Normal products oxirane **8**, dioxole **9**, and dihydrofuran derivatives **10** expected from the vinyl carbonyl ylide were not formed. Reaction of *p*-tolylvinyldiazomethane **2b** and *t*-butylvinyldiazomethane **2c** with indanetrione gave similar results, giving **7b** and **7c**, respectively, but not oxirane **8b**,**c**, dioxole **9b**,**c**, and dihydrofuran derivatives **10b**,**c**. The NMR spectra of **7b**,**c** showed a very similar pattern to that of **7a**, except for the signals of the R group.[11]

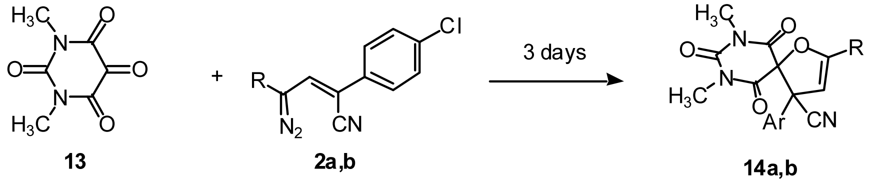
The mechanism for formation of **7** is shown in Scheme 2. Vinyl diazo compound **2** underwent 1,3-dipolar cycloaddition with the electron-deficient central carbonyl group of indanetrione **1** to give the oxadiazoline **3**, which eliminated nitrogen to give the vinyl carbonyl ylide **4** bearing the bulky substituent R at the *exo*-position. The (*Z*)-cyanostyryl moiety of carbonyl ylide **4** isomerized to the sterically less stable (*E*)-cyanostyryl carbonyl ylide **5** without normal cyclization to oxirane **8** and dioxole **9**. The (*E*)-cyanostyryl carbonyl ylide **5** cyclized to dihydrooxepin **6** via herical transition state (conrotatory mode as an eight-electron system) followed by a 1,5-hydrogen shift to give the spirodihydrooxepin **7**. Isomerization of **4** to **5** can take place by two possible mechanisms: (1) simple rotation around double bond of (*Z*)-cyanostyryl group, and (2) cyclization of **4** to dihydrofuran **10** followed by ring opening to **5** in disrotatory mode as a six-electron system. In order to investigate which mechanisms proceed, the reaction of **1** and **2a** was carried out in $CDCl_3$ at 0°C. A $CDCl_3$ solution of **2a** was added to **1** suspended in $CDCl_3$ and 3 h later, the NMR spectrum of the reac-



Scheme 2.



Scheme 3.



Scheme 4.

tion mixture showed a singlet at δ 5.29, which gradually disappeared. The singlet (δ 5.29) seems to be due to the vinylic proton of **10a**. Observation of signals of **10a** suggests the possibility that **4** isomerizes to **5** via **10**.

In order to investigate effects of the ring size of triketone on the cyclization mode of the vinyl carbonyl ylides, the reactions of **2** with six-membered cyclic tricarbonyl compounds were carried out, giving quite different results. The reaction of **2a** with the six-membered triketone **11** did not yield dihydrooxepin derivatives, but the dioxole **12** in 92% yield (Scheme 3).[12] Formation of dioxoles have been known in the reaction of **11** with diazomethane,[13] diphenyldiazomethane, and diazofluorene.[9] Another six-membered tricarbonyl compound dimethylalloxane **13** was reacted with **2a** and **2b** to give dihydrofurans **14a** and **14b**,[14] respectively, which are typical products of vinylcarbonyl ylides (Scheme 4).

In the reaction of indanetriketone, other possible products, such as oxiranes **8**, dioxoles **9**, and dihydrofurans **10**, seem to be either difficult to form due to steric reasons or are electronically unstable because of ring-opening reactions equilibriating with the carbonyl ylide intermediates.

In summary, we describe in this paper the first example of generation of vinyl carbonyl ylides via extrusion of nitrogen from Δ^3-1,3,4-oxadiazoline formed by the 1,3-dipolar cycloaddition reaction of tricarbonyl compounds with vinyldiazo compounds **2** and that the vinyl carbonyl ylide from the reaction of indanetrione with the vinyldiazo compounds **2a**,**b**,**c** underwent abnormal 1,7-cyclization of the vinyl carbonyl ylides to give spiroindan-1,3-dione-2,2′-benzodihydrooxepin **7a**,**b**,**c**.

References

1. (a) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223; (b) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091; (c) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263; (d) Osterhut, M. H.; Nadler, W. R.; Padwa, A. *Synthesis* **1994**, 123.
2. (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 572; (b) Lipson, M.; Noll, B. C.; Peters, K. S. *J. Org. Chem.* **1997**, *62*, 2409; (c) Clawson, P.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1193; (d) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 159; (e) Clawson, P.; Lunn, P. M.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 153; (f) Albini, A.; Arnold, D. R. *Can. J. Chem.* **1978**, *56*, 2985; (g) Ishikawa, K.; Griffin, G. W.; Lev, I. J. *J. Org. Chem.* **1976**, *41*, 3747; (h) Volatron, F.; Anh, N. T.; Jean, Y. *J. Am. Chem. Soc.* **1983**, *105*, 2359; (i) Linn, W. J.; Benson, R. E. *J. Am. Chem. Soc.* **1965**, *87*, 3657.
3. (a) Rigby, J. H.; Danca, M. D. *Tetrahedron Lett.* **1999**, *40*, 6891; (b) Sharma, P. K.; Warkentin, J. *Tetrahedron Lett.* **1995**, *36*, 7591; (c) Couture, P.; Terlouw, J. K.; Warkentin, J. *J. Am. Chem. Soc.* **1996**, *118*, 4214.
4. (a) Padwa, A.; Hasegawa, T.; Liu, B.; Zhang, Z. *J. Org. Chem.* **2000**, *65*, 7124; (b) Kitagaki, S.; Yasugahira, M.; Anada, M.; Nakajima, M.; Hashimoto, S. *Tetrahedron Lett.* **2000**, *41*, 5931; (c) Hodgston, D. M.; Villalonga-Barber, C. *Tetrahedron Lett.* **2000**, *41*, 5597; (d) Kitagaki, S.; Anada, M.; Kataoka, O.; Matsuno, K.; Umeda, C.; Waanabe, N.; Hashimoto, S. *J. Am. Chem. Soc.* **1999**, *121*, 1417; (e) Kataoka, O.; Kitagaki, S.; Watanabe, N.; Kobayashi, J.; Nakamura, S.; Shiro, M.; Hashimoto, S. *Tetrahedron Lett.* **1998**, *39*, 2371; (f) Padwa, A.; Price, A. T. *J. Org. Chem.* **1998**, *63*, 556; (g) Hamaguchi, M.; Ibata, T. *Tetrahedron Lett.* **1974**, *15*, 4475.
5. (a) Hudlicky, T.; Barbieri, G. *J. Org. Chem.* **1991**, *56*, 4598; (b) Eberbach, W.; Burchardt, B. *Chem. Ber.* **1978**, *111*, 3665.
6. (a) Hamaguchi, M.; Matsubara, H.; Nagai, T. *J. Org. Chem.* **2001**, *66*, 5395; (b) Hamaguchi, M.; Matsubara, H.; Nagai, T. *Tetrahedron Lett.* **2000**, *41*, 1457; (c) Anac, O.; Daut, A. *Liebigs Ann./Recl.* **1997**, 1249.
7. (a) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 4260; (b) Advani, B. G. *Tetrahedron Lett.* **1967**, *8*, 2689.
8. Schönberg, A.; Junghans, K. *Chem. Ber.* **1963**, *96*, 3328.
9. Schönberg, A.; Singer, E. *Chem. Ber.* **1972**, *105*, 2246.
10. Crystallographic data for compound **7a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC

202765. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

11. ^{1}H NMR spectrum of **7a** ($CDCl_3$): δ 8.12–8.03 (m, 2H), 7.97–7.91 (m, 2H), 7.90 (d, 1H, $J=8.6$ Hz), 7.44 (d, 1H, $J=2.0$, 8.6 Hz), 7.36–7.30 (m, 5H), 7.25 (d, 1H, $J=4.6$ Hz), 6.87 (d, 1H, $J=2.0$ Hz), 5.77 (d, 1H, $J=4.6$ Hz). **7b**: δ 8.13–8.04 (m, 2H), 7.99–7.91 (m, 2H), 7.90 (d, 1H, $J=8.6$ Hz), 7.44 (d, 1H, $J=2.0$, 8.6 Hz), 7.26 (d, 1H, $J=4.6$ Hz), 7.24 (d, 2H, $J=8.2$ Hz), 7.16 (d, 2H, $J=8.2$ Hz), 6.85 (d, 1H, $J=2.0$ Hz), 5.82 (d, 1H, $J=4.6$ Hz), 2.32 (s, 3H). **7c**: δ 8.16–8.06 (m, 2H), 8.00–7.97 (m, 2H), 7.82 (d, 1H, $J=8.6$ Hz), 7.41 (d, 1H, $J=2.0$, 8.6 Hz), 7.20 (d, 1H, $J=5.3$ Hz), 6.78 (d, 1H, $J=2.0$ Hz), 4.39 (d, 1H, $J=5.3$ Hz), 0.91 (s, 9H).
12. ^{1}H NMR spectrum of **12**: δ 8.71 (d, 1H, $J=7.6$ Hz), 8.23 (d, 1H, $J=7.6$ Hz), 8.13 (d, 1H, $J=7.9$ Hz), 8.07 (d, 1H, $J=7.9$ Hz), 7.87–784 (m, 2H), 7.76 (dd, 1H, $J=7.6$, 7.9 Hz), 7.68 (dd, 1H, $J=7.6$, 7.9 Hz), 7.54 (d, 2H, $J=8.6$ Hz), 7.52–7.48 (m, 3H), 7.38 (d, 2H, $J=8.6$ Hz), 7.10 (s, 1H).
13. Moubasher, R.; Awad, W.; Ibrahim, M.; Abdel, M. O. *J. Chem. Soc.* **1950**, 1998.
14. ^{1}H NMR spectrum of **14b**: δ 7.62 (d, 2H, $J=8.2$ Hz), 7.39 (s, 4H), 7.25 (d, 2H, $J=8.2$ Hz), 5.37 (s, 1H), 3.48 (s, 3H), 2.67 (s, 3H), 2.42 (s, 3H).