Pergamon

Tetrahedron Letters 39 (1998) 5627–5630

TETRAHEDRON
LETTERS

Novel 1,3-Dipolar Cycloaddition Reaction of Carbonyl Ylide with *o*-Quinones[#]

Vijay Nair,*[a] K. C. Sheela,[a] K. V. Radhakrishnan,[a] Nigam P. Rath[b]

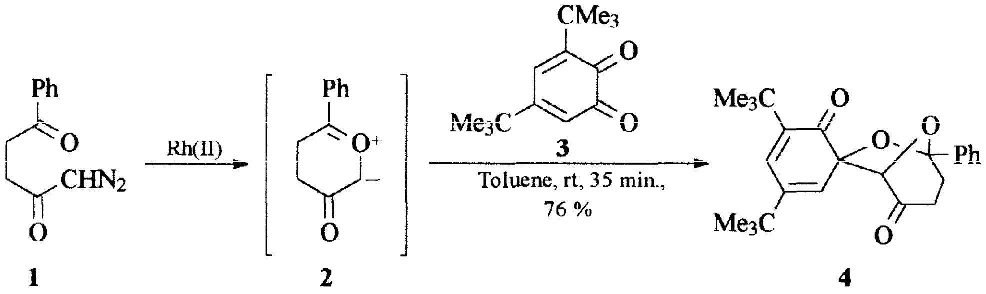
a Organic Chemistry Division, Regional Research Laboratory (CSIR), Trivandrum-695 019, INDIA
b. Department of Chemistry, University of Missouri-St. Louis, Missouri 63121-4499, U. S. A.

Received 20 February 1998; revised 18 May 1998; accepted 22 May 1998

Abstract: 1,3-Dipolar cycloaddition reaction of carbonyl ylide with *o*-quinones afforded novel highly oxygenated spirocyclic compounds.

During the course of our work on the Diels-Alder reactions of *o*-quinones,[1,2] we became aware that the dipolar cycloaddition reactions of the latter have received very little attention.[3] The scant information available in this area is derived from the reaction of diazomethane with 3,6-di-*tert*-butyl-1,2-benzoquinone[4] and the reaction of certain mesoionic compounds with *o*-chloranil.[5,6] Very recently we have observed that aryl nitrile-N-oxides undergo facile cycloaddition to the carbonyl group of *o*-benzoquinones, resulting in 1,3,5-spirodioxazolines.[7]

As a part of our continuing interest in probing the dipolarophilic profile of *o*-quinones, we have undertaken some work on their reaction with carbonyl ylide dipole and our preliminary results displaying a novel cycloaddition are presented here.It is noteworthy that although Padwa has studied [8] the reactions of carbonyl ylides with benzaldehyde and other aldehydes, as far as we know, no work on the addition of carbonyl ylides to quinones has been reported by anyone. Our studies were initiated with Rh(II) catalyzed cycloaddition of 1-diazo-5-phenyl-2,5-pentanedione **1** to 3,5-di-*tert*-butyl-1,2-benzoquinone **3**. This reaction proceeded smoothly to afford the product **4** [Scheme 1].[9]



1 **2** **3** **4**

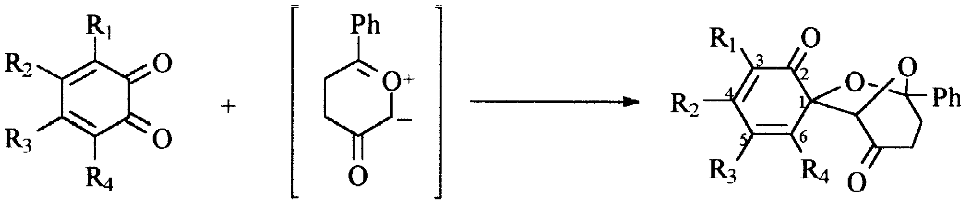
Scheme 1

[#] *Dedicated with warm personal regards to Professor Paul Wender*

0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)01065-X

The product was purified using Chromatotron (silica gel, Merck, TLC grade 7749) and characterized by spectral analysis.[10] The IR spectrum of **4** showed two carbonyl absorptions at 1708 and 1735 cm^{-1}. In ^{1}H NMR, the bridgehead proton resonated at δ 4.58. In ^{13}C NMR spectrum of **4**, the characteristic signal for the spiro carbon was observed at δ 110.51. Final proof for the structure **4** was derived by single crystal X-ray analysis.[11]

The experiment was repeated with various *o*-quinones and in all cases the reaction proceeds smoothly to afford the product. The results are summarized in Table 1.



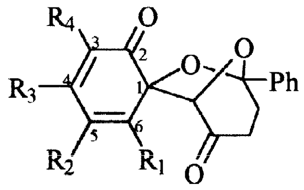
3 (a-e) **2** **4 (a-e)**

Table 1. Cycloaddition of carbonyl ylide with *o*-Quinones.

Entry	Quinone	Substituents	Product	Yield (%)[a]	M.P
1	**3a**	$R_1 = R_2 = R_4 = H, R_3 = -CMe_3$	**4a**	42*	44-46 °C
2	**3b**	$R_1 = R_3 = -CMe_3, R_2 = H, R_4 = -OMe$	**4b**	61	169-170 °C
3	**3c**	$R_1 = R_2 = H, R_3 = -CMe_3, R_4 = -OMe$	**4c**	48	164-166 °C
4	**3d**	$R_1 = R_3 = CHPh_2, R_2 = H, R_4 = -OMe$	**4d**	41*	181-183 °C
5	**3e**	$R_1 = R_2 =$ Benzo, $R_3 = R_4 =$ Benzo	**4e**	37	158-160 °C

[a] Isolated yield; *15 % of a product tentatively identified as a 2:1 adduct of 2 and 3 was also isolated.

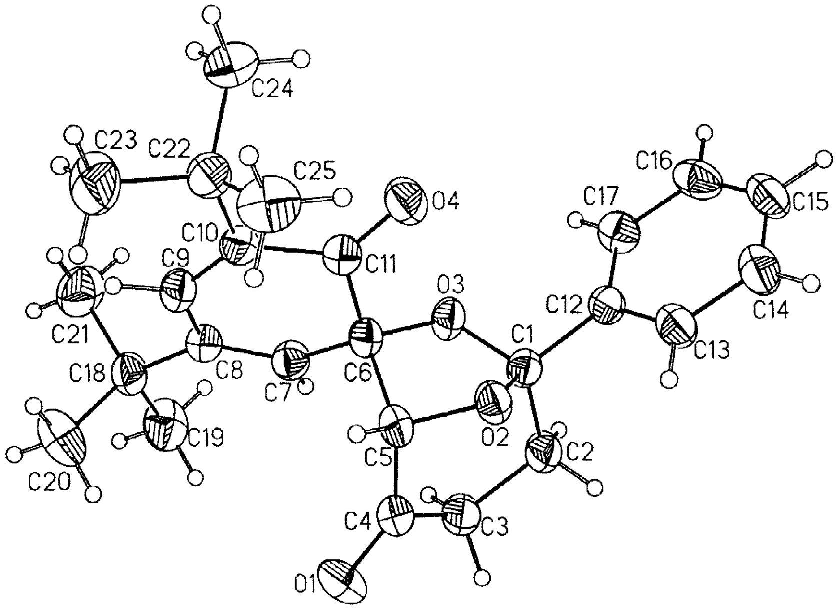
The structures of **4a-4e** were assigned on the basis of spectral data, especially by comparing ^{1}H NMR data with that of **4**. For instance C_6-H in **4a** resonates at δ 5.92 and the C_4-H at δ 7.09. These chemical shifts compare favourably with those of the corresponding protons in **4**; C_6-H resonates at δ 5.85 and C_4-H at δ 6.76. Furthermore in the alternative structure (**4'a-e**) resulting from the addition of the ylide to the other carbonyl group, the corresponding protons (C_3-H and C_5-H) will be expected to resonate at significantly



(4'a-e)

higher fields. Similar analysis of the ^{1}H NMR data leads to the reasonable conclusion that the assigned structures are correct. Interestingly in all the cases the ylide preferentially adds to the more electron deficient of the two carbonyls of each quinone. Such preference is precedented in the reactivity of dicarbonyl compounds towards dipolar species.[7]

In conclusion, it has been shown that carbonyl ylide dipole undergoes facile cycloaddition to *o*-quinones, thus offering an efficient method for the synthesis of novel highly oxygenated heterocyclic compounds. It is anticipated that the products of the cycloaddition themselves will be potentially amenable to a number of interesting and possibly useful transformations. Further work is in progress.



X-ray Structure of **4**

ACKNOWLEDGEMENTS

The authors thank Dr. Jaya Prabhakaran, ICSN, CNRS, France for elemental analysis. KCS and KVR thank CSIR, New Delhi for research fellowships.

REFERENCES AND NOTES

1. (a) Nair, V.; Kumar, S. *Synlett* **1996**, *12*, 1143 and references cited therein. (b) Nair,V.; Kumar,S.; Rath, N. P.; Morton, G. O. *Chem. Lett.* **1995**, 383. (c) Nair, V.; Kumar, S.; Anilkumar, G.; Nair, J. S.

Tetrahedron **1995**, *51*, 9155. (d) Nair, V.; Kumar, S. *J. Chem. Soc., Perkin Trans. 1* **1996**, 443. e). Nair, V.; Kumar, S. *Synth. Commun.* **1996**, *26*, 217.

2. For earlier work on the Diels -Alder reactions of *o*-quinones see, Patai, S.; Rappoport, Z. In *The Chemistry of Quinonoid Compounds*, Vol. 2, John Wiley & Sons, New York, **1988**.
3. Padwa, A. In *1,3-Dipolar Cycloaddition chemistry*, Wiley-Interscience, New York, **1984**.
4. Kommissarova, N. L.; Belostotskaya, I. S.; Vol'eva, V. B.; Dzhuaryan, E. V.; Novikova I. A.; Ershov V.V. *Izv.Akad. Nauk. SSSR, Ser.Khim (Eng.Trasl.)* **1981**, 2360.
5. (a) Friedrichsen, W.; Schröer, W. D.; Debaerdemaeker,T. *Justus Liebigs Ann. Chem.* **1980**, 1850; (b) Friedrichsen, W.; Schröer, W. D.; Debaerdemaeker, T. *Justus Liebigs Ann. Chem.* **1980**, 1836. (c) Lawson, A.; Miles, D. H. *J. Chem. Soc.* **1959**, 2865; *Ibid* **1960**, 1945.
6. (a) Friedrichsen, W.; Krüeger, C.; Kujath, E.; Liebezeit, G.; Mohr, S. *Tetrahedron Lett.* **1979**, 237. (b) Friedrichsen, W.; Schmidt, R.; van Hummel. G. J.; van den Ham, D. M. W. *Ann.* **1981**, 521; (c) Friedrichsen, W.; Kappe,T.; Böttcher, A. *Heterocycles* **1982**, *19*, 1083.
7. Nair, V.; Radhakrishnan, K. V.; Nair, A. G.; Bhadbhade, M. M. *Tetrahedron Lett.* **1996**, *37*, 5623.
8. Padwa, A.; Fryxel, G. E.; Zhi, L. *J. Am.Chem. Soc.* **1990**, *112*, 3100.

9. Typical experimental procedure: 3,5-Di-*tert*-butyl-1,2-benzoquinone **3** (0.220 g,1 mmol) was added to a solution of 1-diazo-5-phenyl-2,5-pentanedione **1** (0.243 g, 1.2 mmol) and Rh(II)acetate (catalytic amount) in dry toluene (8 mL) at room temperature under argon atmosphere and stirred. When the reaction was complete (as indicated by TLC, 35 min.), the solvent was evaporated *in vacuo*. The residue obtained was purified using a chromatotron (silica gel, Merck, TLC grade, 7749). Elution with 1% ethyl acetate in hexane afforded **4** (0.297 g, 76%) as pale yellow crystalline solid (m.p 208-209 °C).
10. Spectral data for illustrative example **4**. IR (KBr): 2955, 1735, 1708, 1640, 1458, 1371, 1276, 1128, 1074, 1040, 960, 946, 885, 778, 703 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.42 (5H, Ar), 6.76 (d, J = 2.1 Hz, 1H), 5.84 (d, J =2.1 Hz, 1H), 4.58 (s, 1H), 2.64-2.62 (m, 4H), 1.18 (s, 9H), 1.11 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$). δ 201.85, 199.33, 147.49, 144.75, 138.72, 133.69, 128.70, 128.20, 125.29, 122.54, 110.51, 87.90, 82.08, 35.67, 34.56, 33.26, 29.25, 28.38. CHN analysis: Found: C-75.61%, H-7.95%. (Calculated: C-76.11%, H-7.66%).
11. Crystal data for **4**: $C_{25}H_{30}O_4$ F.W: 394.49; 0.38x0.30x0.22mm, Triclinic, Space group P$\bar{1}$ Unit cell dimensions a =5.9075(1)Å, α = 97.315(1)°; b = 9.7892(1)Å, β = 97.692 (1)°; c = 19.2052 (2) Å ; γ = 91.79°, R indices (all data) RI = 0.0860, wR2 = 0.1427. Volume, Z = 1090.36 (2) Å^3, 2, D calc. = 1.202 Mg/m^3. F (000) = 424. Absorption coefficient = 0.080 mm^{-1}; Reflections collected = 20474. (Sheldrick, G. M.. Siemens, Analytical X-ray Division, Madison, WI, **1995**).