1,3-Dipolar Cycloreversion of the 1-Pyrazoline from 5-Diazo-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene and 2,5-Dimethyl-1,4-benzoquinone

Takumi Oshima* and Toshikazu Nagai

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Machikaneyama 1-16, Toyonaka, Osaka 560, Japan

Thermolysis of the pyrazoline formed from 5-diazo-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene and 2,5-dimethyl-1,4-benzoquinone gives the component diazoalkane and quinone *via* 1,3-dipolar cycloreversion, in competition with nitrogen extrusion to give the cyclopropane derivative.

1,3-Dipolar cycloreversions are a small part of the large field of studies of 1,3-dipolar cycloadditions.[1] This cleavage of two σ bonds of five-membered heterocycles is generally induced thermally, photochemically, or by electron impact.[1] However, probably owing to thermodynamic reasons, the reported examples of true 1,3-dipolar cycloreversions releasing the starting reactants are much more rare.[2] Therefore, it is desirable to find out the dipole–dipolarophile couple which is most conveniently equilibrated with the dipolar adduct, and to shed light on the mechanistic features of such retroaddition.

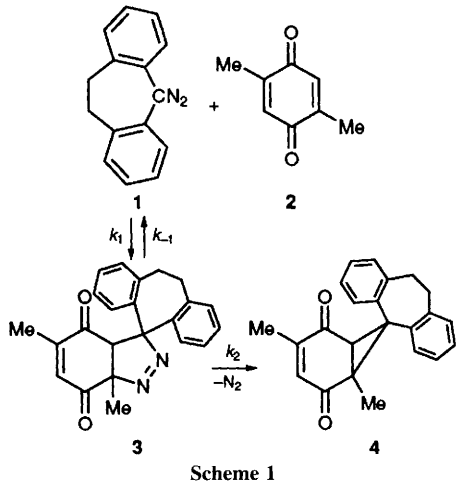
We now report that thermolysis of the 1-pyrazoline **3** from 5-diazo-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene **1** and 2,5-dimethyl-1,4-benzoquinone **2** results in 1,3-dipolar cycloreversion and nitrogen extrusion to give the starting dipole–dipolarophile couple and the cyclopropane derivative **4**, respectively (Scheme 1). In particular, this report deals with the kinetic solvent effects as a mechanistic criterion of the retroaddition.

Reaction of **1** (650 mg, 2.95 mmol) with 1 equiv. of **2** (400 mg, 2.94 mmol) at room temp. for 2 days produced pyrazoline **3** (701 mg, 66.7%) and cyclopropane **4** (196 mg, 20.3%) together with some unreacted **1** (25 mg) and **2** (37 mg) in benzene (4 ml) (Scheme 1). Although quite stable in the pale-yellow crystalline state for several months at −18 °C, **3** was found to revert to **1** and **2** at 50 °C in competition with the degradation into **4**, as confirmed by NMR spectroscopy. Accordingly, the overall process for the reaction of **1** and **2** can be shown as in Scheme 1.

The ^{1}H NMR monitoring of equimolar reaction of **1a** and **2** under high concentrations (5.20×10^{-1} mol dm^{-3}) gave the equilibrium constant K ($= k_1/k_{-1}$) of 2.02 dm^3 mol^{-1} (50 °C, C_6D_6) based on the concentrations of relevant **1**, **2** and **3**; the equilibration was attained over 60% conversion. The value of K is so small that the equilibrium lies far to the left in rather dilute solution. Under such conditions, thermal degradation of **3** should follow the combined first-order reaction rate, (k_{-1} + k_2) [**3**], since the second-order rate of the reverse reaction ($= k_1$ [**1**] [**2**], here [**1**] = [**2**]) of the generated pyrolysates **1** and **2** is negligibly small. In fact, thermolysis of **3** in low concentration (<10^{-2} mol dm^{-3}) obeyed a simple first-order rate law over second halflives.

Thermolysis of **3** was performed in NMR tubes. The detectable products were **1**, **2** and **4**, together with the reactant **3** and the compositions of these reaction mixtures were determined on the basis of the integral ratios of their methyl signals at intervals by ^{1}H NMR analysis. The observed first-order rate constants, k_{obs} ($= k_{-1} + k_2$), for the disappearance of **3** in a wide variety of solvents at 50 °C are given in Table 1, together with the product ratios (**2**:**4**) and the distributed rate constants, k_{-1} and k_2, for the cycloreversion and nitrogen extrusion processes.

Cycloreversion predominated over nitrogen extrusion in all solvents tested (k_{-1}/k_2 = 1.2–3.2). The solvent dependencies



Scheme 1

Table 1 Kinetic study of the thermolysis of **3** in various solvents at 50 °C.

Solvent	k_{obs}/ 10^{-5} s^{-1}	k_{-1}/ 10^{-5} s^{-1} [a]	k_2/ 10^{-5} s^{-1} [a]	Product ratio **2**/**4** [b]	E_T	$D\pi$
[^{2}H]Acetic acid	18.3	12.1	6.20	1.95	51.2	—
[^{2}H]Chloroform	17.6	13.3	4.33	3.06	39.1	−1.56
[$^2H_2$]Dichloromethane	12.9	8.82	4.08	2.16	41.1	−1.30
Bromobenzene	12.5	9.41	3.09	3.05	37.5	−1.03
[$^2H_4$]Methanol	11.9	8.11	3.79	2.14	55.5	—
Chlorobenzene	11.8	8.98	2.82	3.19	37.5	−0.903
Fluorobenzene	10.8	7.62	3.18	2.40	38.1	−0.818
Carbon tetrachloride	10.8	7.73	3.07	2.52	32.5	—
[$^2H_6$]Benzene	9.71[c]	6.75	2.96	2.28[c]	34.5	0
[$^2H_5$]Pyridine	8.40	5.58	2.82	1.98	40.4	—
Ethyl acetate	8.22	5.40	2.82	1.92	38.1	0.289
[$^2H_3$]Acetonitrile	6.51	3.69	2.82	1.31	46.0	−0.440
[$^2H_8$]Tetrahydrofuran	6.47	4.13	2.34	1.77	37.5	0.639
[$^2H_6$]Acetone	6.20	3.38	2.82	1.20	42.2	0.261
[$^2H_6$]Dimethyl sulfoxide	4.70	2.58	2.12	1.22	45.0	—

[a] Individual rate constants were calculated from the observed first-order rate constants, k_{obs}, and the product distribution; k_{-1}/k_2 being set equal to the ratio **2**:**4**. [b] Average of at least five individual values. [c] The k_{obs} ($\times 10^5$) values and the product ratio at different temperatures were: 2.47 (**2**:**4** = 2.32) at 40 °C, 5.12 (2.29) at 45 °C, 18.4 (2.30) at 55 °C, and 35.9 (2.28) at 60 °C.

of k_{-1} and k_2 are so small that the total range amounts to only a factor of 5.5 for k_{-1} and 2.9 for k_2 over the wide range of solvent polarities investigated.

The small solvent polarity effect on cycloreversion indicates concerted bond cleavage through the non-polar transition state (TS). Such decomposition to diazoalkane and quinone fits the orbital symmetry requirements for the concerted bond changes.[3] Noticeably, though not a true 1,3-dipolar cycloreversion, Warkentin *et al.*[4] obtained a high rate ratio (k_{MeOH}/k_{CCl_4} = 16) [*i.e.* E_T values: of 55.5 (MeOH) to 32.5 (CCl_4)] for the thermolysis of 5,5-dimethyl-1,3,4-oxadiazolinone into 2-diazopropane and carbon dioxide (84 °C). They rationalized the solvent effect in terms of the polar TS of oxadiazolinone. The corresponding value for the present cycloreversion is only 1.1, probably because of the much less polar TS for **3**.

As for the nitrogen extrusion giving cyclopropane **4**, a simultaneous homolytic cleavage is argued for 1-pyrazolines like **3** with less polar substituents,[6] and the diradical-like TS is consistent with the negligible solvent effects.[7]

The activation parameters at 50 °C in [$^2H_6$]benzene were 112.2 kJ mol^{-1} ($\Delta H^{\ddagger}$) and 21.9 J mol^{-1} K^{-1} ($\Delta S^{\ddagger}$) for cycloreversion and 112.9 and 17.2 for nitrogen extrusion, respectively. The positive values of $\Delta S^{\ddagger}$ in both cases are in good agreement with unimolecular decomposition with a non-polar TS.

Though the effect of the solvent on the rate is small, relations of log k with a combination of empirical solvent polarity and basicity parameters, E_T[5] and D_π[8] are fair (eqns. 1 and 2). The percentage contributions of these parameters are 37% (E_T) and 63% (D_π) for eqn. 1 and 2% and 98% for eqn. 2. Thus, the role of the solvent basicity (D_π) is much more important than its polarity effects (E_T).

$$\log k_{-1} = -0.0321E_T - 0.230D_\pi - 3.04 \quad (r = 0.984,\ n = 10,\ s = 0.039) \qquad (1)$$

$$\log k_2 = -0.000503E_T - 0.0893D_\pi - 4.58 \quad (r = 0.835,\ n = 10,\ s = 0.050) \qquad (2)$$

The dominant parameter D_π has a negative coefficient in both cases. One might expect the rate reduction due to the stabilization of reactant **3** by electron donor solvents. However, the absolute coefficient of D_π for cycloreversion is 2.6 times larger than that for nitrogen extrusion. Relative to **3**, the energy of the transition state for cycloreversion is less stabilised by donor solvents than that for nitrogen extrusion. 1,3-Dipolar cycloaddition is inferred to have a reactant-like TS.[9] If pyrazoline **3** reverts *via* the same TS as dipolar addition, the TS will be sustained by HOMO–LUMO orbital interaction between nascent diazoalkane and quinone **2**. The electron pair donor solvent is expected to weaken the electron affinity of **2** and thereby reduce the energy gain due to the FMO interaction,[10] with the TS being less stabilized. Donor–acceptor interaction of quinone with electron pair donor solvent is quite common.[11]

Received, 30th September 1994; Com. 4/05998K

References

1 G. Bianchi, C. D. Michcli and R. Gandolfi, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 721; G. Bianchi and R. Gandolfi, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 2, p. 451.

2 While not studied in detail, it has been observed by NMR analysis that upon being heated, the minor regioisomer of 1-pyrazolines from bis(*p*-tolyl)diazomethane and carbomethoxy-substituted norbornene derivative reverts to the component reactants: J. W. Wilt, V. A. Curtis and C. O-Yang, *J. Org. Chem.*, 1982, **47**, 3721.

3 R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 781; M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 761.

4 S. L. Lee, A. M. Cameron and J. Warkentin, *Can. J. Chem.*, 1972, **50**, 2326.

5 C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 98; C. Reichardt and E. H;-Görnert, *Liebigs Ann. Chem.*, 1983, 721.

6 H. Meier and K.-P. Zeller, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 835; P. S. Engel, *Chem. Rev.*, 1980, **80**, 99.

7 D. E. McGreer, R. S. McDaniel and M. G. Vinje, *Can. J. Chem.*, 1965, **43**, 1389.

8 T. Oshima, S. Arikata and T. Nagai, *J. Chem. Res.*, 1981, (S) 204, (M) 2518.

9 R. Huisgen, in *1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 1, p. 42.

10 K. N. Houk, in *Pericyclic Reactions*, ed. A. P. Marchband and R. E. Lehr, Academic, London, 1977, vol. 2, p. 181.

11 T. Oshima and T. Nagai, *Tetrahedron Lett.*, 1985, **25**, 4785.