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THERMAL REACTION OF 2,3-DIAZATETRACYCLO[5.3.1.$0^{4,11}$.$0^{6,8}$]UNDECA-2,9-DIENES:$^{1)}$ THE NITROGEN EXTRUSION AND THE MASKED HOMODIENYL-1,5-HYDROGEN SHIFT

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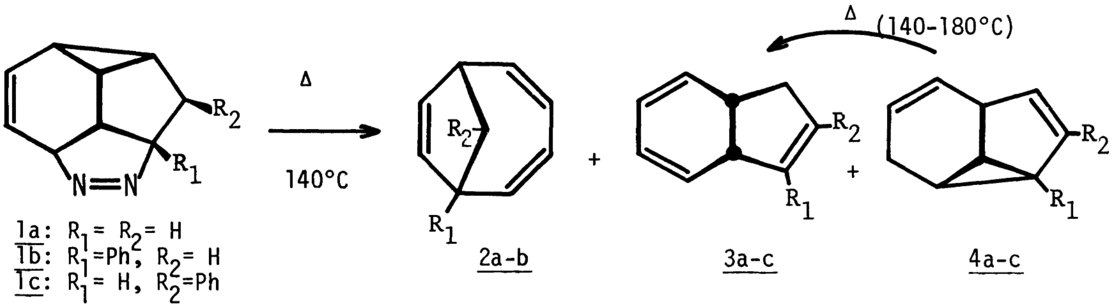
Thermolyses of the title compounds produce three kinds of products which are derived from nitrogen extrusion and 1,5-hydrogen shifts. The reaction mechanism is discussed in connection with the thermal behavior of bicyclo[4.2.1]nonatriene.

The contrast between the thermally and photochemically induced reactions of unsaturated cyclic azo compounds has attracted much attention from a mechanistic view point.$^{2)}$ Recently, we reported the photochemical reaction of the titled compound 1,$^{3)}$ where a retro-1,3-dipolar cycloaddition and a nitrogen extrusion reaction occur competitively. For comparison with the photochemical behavior, the thermal reaction was studied.$^{4)}$ It was found that a homodienyl-1,5-hydrogen shift competed with the nitrogen extrusion process. We present here an outline of the experimental results and discuss the reaction mechanism.



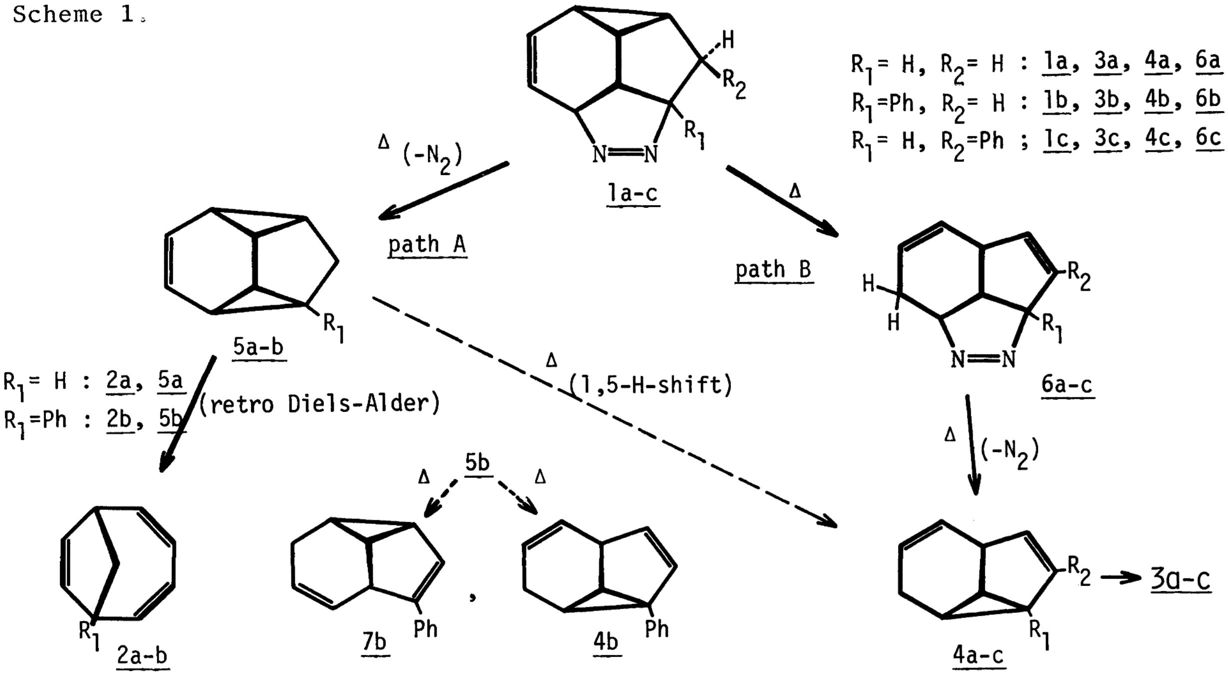
1a: $R_1 = R_2 = H$
1b: $R_1 = Ph$, $R_2 = H$
1c: $R_1 = H$, $R_2 = Ph$

	2a-b	3a-c	4a-c
(3320 min)	2a: 15.3%	3a: 67.5%	4a: 17.2%
(550 min)	2b: 73.4%	3b: 25.4%	4b: 1.2%
(420 min)	2c: ----	3c: 69.2%	4c: 30.7%

The thermolyses of 1a-c$^{3)}$ were carried out at 90-180°C in degassed diglyme solution where three types of products 2a-b, 3a-c, and 4a-c were obtained.$^{5)}$ Among the products, bicyclo[4.2.1]nona-2,4,7-trienes (2a-b) were stable under these thermolysis conditions, while tricyclo[4.3.0.$0^{2,9}$]nona-4,7-dienes (4a-c) were labile on being heated and converted to cis-8,9-dihydroindenes (3a-c) in quantitative yields ($t_{\frac{1}{2}}$ at 140°C ; 4a, 1470 min; 4b, 150 min; 4c, 198 min).

The formation of bicyclo[4.2.1]nonatriene 2 have been rationalized by postulating tetracyclo[4.3.0.0^{2,9}.0^{5,7}]non-3-ene 5 as the precursor. The reaction to tricyclic hydrocarbon 4 might be explained by two routes, i.e., an initial nitrogen extrusion followed by a 1,5-hydrogen shift via tetracyclic nonene 5 (path A) and/or an alternative route via tricyclic pyrazoline 6 generated by an initially preceding 1,5-hydrogen shift (path B). The reaction pathways are summarized in Scheme 1.

Scheme 1.



The following should be noted from the results obtained here; i) With the parent compound 1a, the thermal reaction occurred at higher temperature compared with those of the phenyl derivatives 1b and 1c. The main process was the formation of 4a, although bicyclo[4.2.1]nonatriene was formed in a considerable yield. ii) The thermolysis of 4-phenyl derivative (1b) gave the triene 2b as a major product, and the formation of tricyclic hydrocarbon 4b was a minor process. Another plausible isomer, 7-phenyl derivative (7b) of tricyclo[4.3.0.0^{2,9}]nonadiene, which was expected to originate from the tetracyclic intermediate 5b,6) was not detected at all. In this connection, Carpenter suggests that the formation of 7b was more favored than that of 4b by 7.8 kcal/mol.7) iii) The thermolysis of 5-phenyl derivative (1c) gave tricyclic hydrocarbon 4c unaccompanied by the triene 2c.

All these findings can be explained by the proposal that the homodienyl-1,5-hydrogen shift of tetracyclo[4.3.0.0^{2,9}.0^{5,7}]nonene 5 leading to tricyclo[4.3.0.0^{2,9}]nonadiene 4 does not occur.6) This thermal reaction is interpreted by the path B that tricyclo[4.3.0.0^{2,9}]nonadiene and cis-8,9-dihydroindene originate from the alternative precursor 6. On the other hand, the tetracyclo[4.3.0.0^{2,9}.0^{5,7}]-nonenes (5a and 5b) generated by these thermolyses are considered to give bicyclo-

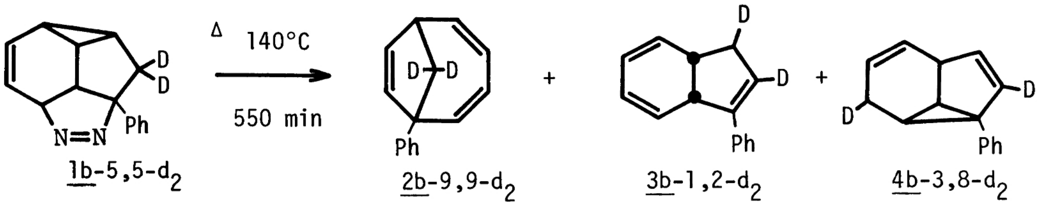
[4.2.1]nonatrienes 2a-b exclusively. Thus, in the case of 1b, the phenyl group at the C_4-position accelerates N-C_4 bond cleavage and then increases the ratio of 2b. The C_5-phenyl group of 1c activates the 1,5-hydrogen shift leading to pyrazoline 6c because the hydrogen is located in a benzylic position. As a result, the formation of 4c becomes predominant. Actually, when the thermolysis of 1c was carefully carried out at 120°C, the tricyclic pyrazoline 6c could be successfully isolated in 12% yield.8)

In order to confirm the mechanism of these thermal reactions, kinetic studies and deuterium labelling experiments were performed. At first, it is noted that the ratios of the products are temperature dependent: 2a/(3a+4a)= 0.176 at 140°C, 0.527 at 180°C, and 3.59 at 280°C; 2b/(3b+4b)= 1.53 at 140°C, 3.33 at 180°C, and 11.2 at 280°C. The activation parameters are shown in Table 1. These values rationalize the phenyl substituent effect mentioned above.

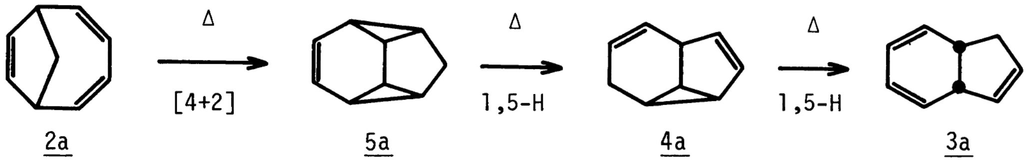
Table 1. Activation Parameters for the Formations of 2a-b, 4a-b, and 6c.9)

	1a to 2a	1a to 4a	1b to 2b	1b to 4b	1c to 6c
Activation Enthalpy (kcal/mol)	43.5 ± 0.2	33.0 ± 0.6	33.4 ± 0.1	24.6 ± 0.1	23.2 ± 0.4
Activation Entropy (e.u.)	19.9 ± 0.6	-5.4 ± 0.4	3.0 ± 0.3	-20.4 ± 0.4	-18.8 ± 0.8

When the D-labelled 4-phenyl derivative (1b-5,5-d_2)10) was thermolyzed at 140°C, three products, 2b-9,9-d_2, 3b-1,2-d_2 and 4b-3,8-d_2, were obtained in 89.5%, trace, and 10.3% yields. The labelled position in these products is consistent with the reaction mechanism. The observed isotope effect k^H/k^D= 3.4 is also reasonable as a primary one. Even though the tricyclic pyrazolines could not be detected in the thermolyses of 1a-b, we wish to propose the pyrazolines 6a-b as the precursors of tricyclic hydrocarbons 4a-b.



Berson reported the high-temperature thermolysis of bicyclo[4.2.1]nonatriene (2a) leading to 3a, and proposed a hydrogen rebound mechanism (two successive 1,5-hydrogen shifts) which is composed of the sequence of steps 2a → 5a → 4a → 3a.6) It was shown that the tetracyclo[4.3.0.$0^{2,9}$.$0^{5,7}$]nonene 5 isomerized to give bicyclo[4.2.1]nonatriene 2 under these reaction conditions. Now we have no evidence for the homodienyl-1,5-hydrogen shift of 5 to 4. However, this is not directly imcompatible with the hydrogen rebound mechanism, if the 1,5-hydrogen shift of 5 leading to 4 has a high energy barrier.



In summary, it is emphasized that the tetracyclic azo compound 1 undergo homodienyl-1,5-hydrogen shift and nitrogen extrusion competitively. This is a novel phenomenon in the thermal behavior of unsaturated azo compounds.11) We are grateful to Professors J.A. Berson and B.K. Carpenter for their valuable advice and discussion for this work.

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5) All products were characterized from the spectral properties and compared with the authentic samples. 2a: T. Tsuruta, K. Kurabayashi and T. Mukai, Tetrahedron Lett., 1967, 3775; 2b3); 3a: S.T. Cantrell and H. Shechter, J. Am. Chem. Soc., 89, 5868 (1967); 3b: NMR(CCl_4) δ 2.43(H_{1a}, d d d d), 2.83(H_{1b}, d d d), 3.15 (H_8, d d d), 4.06(H_9, br d), 5.6-5.85(H_{4-7}, m), 7.1-7.5(5H, Ph), $J_{1a,1b}$= 16.0, $J_{1a,2}$= 2.3, $J_{1a,8}$= 8.4, $J_{1a,9}$= 2.3, $J_{1b,2}$= 3.0, $J_{1b,8}$= 8.0, $J_{2,9}$= 1.7, $J_{8,9}$= 11.5 Hz; 4c: NMR(C_6D_6) δ 2.3-3.2(3H, m), 3.53(H_9, br d), 5.3-6.0(4H, m), 7.0-7.4(5H, Ph), $J_{8,9}$= 11.5 Hz; 4a was synthesized from benzoic acid6); 4b: NMR($CDCl_3$) δ 1.55-2.05(3H, m), 2.58(H_{3b}, d d d d), 3.75(H_6, d d d), 4.95(H_8, d d d), 5.8-5.95(3H, m), 7.0-7.4(5H, Ph), $J_{1,2}$= 9.0, $J_{1,6}$= 7.2, $J_{1,7}$= 1.2, $J_{2,3a}$= 2.6, $J_{3a,3b}$= 17.5, $J_{3a,4}$= 1.6, $J_{3b,4}$= 4.0, $J_{3b,5}$= 2.0, $J_{5,6}$= 7.6, $J_{6,7}$= 2.0, $J_{7,8}$= 5.4 Hz; 4c: NMR($CDCl_3$) δ 1.3-1.55(H_2 and H_{3a}, m), 1.73(H_1, d d d d), 2.16(H_9, d d), 2.48(H_{3b}, d d), 3.76(H_6, d d d), 5.20(H_7, m), 5.7-6.0 (H_4 and H_5, m), 7.1-7.45(5H, Ph), $J_{1,2}$= 7.2, $J_{1,6}$= 7.2, $J_{1,7}$= 0.9, $J_{1,9}$= 6.8, $J_{2,3b}$= 9.2, $J_{2,9}$= 6.8, $J_{3a,3b}$= 6.7, $J_{3a,4}$= 1.4, $J_{5,6}$= 7.0, $J_{6,7}$= 2.4 Hz.

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7) B.K. Carpenter (Cornell University), private communication. He has estimated the difference by HMO treatment. cf.) Tetrahedron, 34, 1877 (1978).

8) The isolated primary product 6c gave 5c on being heated in quantitative yield. Pyrazoline 6c: $C_{15}H_{14}N_2$, mp 83.5-84°C; IR (KBr) 3090, 3070, 3030, 2960, 1600, 1498, 1447, 756, 693 cm^{-1}; NMR(C_6D_6) δ 2.0-2.5(H_{10a} and H_{11}, m), 2.75(H_7, m), 3.07(H_{10b}, d d d), 4.05(H_1, d d d d), 5.37(H_4, d d d), 5.63(H_6, d d), 7.0-7.3 (2H, Ph), 7.8-8.0(3H, Ph), $J_{1,4}$= 2.1, $J_{1,10a}$= 7.1, $J_{1,10b}$= 2.2, $J_{1,11}$= 8.7, $J_{4,6}$= 1.5, $J_{4,11}$= 9.0, $J_{6,7}$= 3.0, $J_{7,11}$= 9.0, $J_{9,10b}$= 2.2, $J_{10a,10b}$= 16.5 Hz; UV(cyclohexane) λmax= 219.4 (ε 1,290), 256.4 (12,700), 340 nm (sh, 192).

9) The formations of 2a-b and 4a-b were measured at four different temperatures (140.0-180.0°C for 1a; 130.0-160.0°C for 1b). The rate constants for 1c were determined by the disappearance of starting material at 125.0-160.0°C.

10) Azo comound 1b-5,5-d_2, which was replaced by deuterium at the C_5-position was synthesized from the tosylhydrazone of the corresponding aryl ketone. The C_5-protons were deuterated in 88%.

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