# Thermolysis of 7-Phenyl-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-dione



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Thermolysis of the title compound in boiling xylene (138°) produces a 7.7/10.1/1.0 mixture of the *N*-phenylimides of *cis*-1,2-cyclopropanedicarboxylic acid, citraconic acid, and itaconic acid. The imides of citraconic and itaconic acids are produced by hydrogen shifts. A completely concerted mechanism involving simultaneous hydrogen shift and cleavage of both C-N bonds is unlikely in the present case because both hydride-shift products are formed and because the optimal arrangement for the hydrogen shift requires deformation of the imide ring and loss of imide resonance. The C-N bond strengths in the title compound should be quite different. The products can arise either from two parallel pathways involving nitrogen-containing dipoles or from a single nitrogen-free trimethylene fragment.

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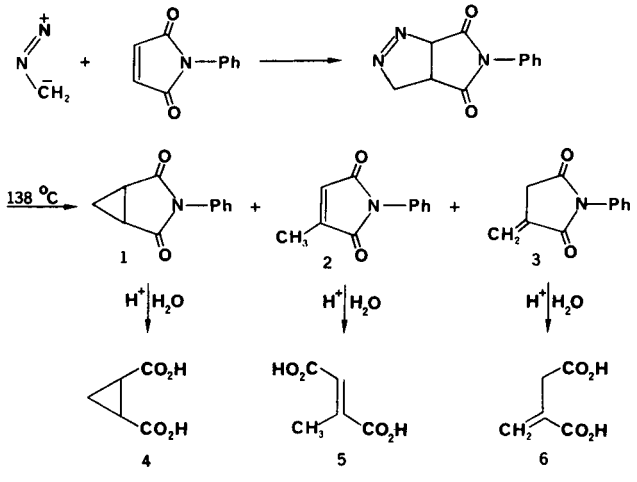
Thermolysis or photolysis of 1-pyrazolines has been the subject of numerous mechanistic studies [2]. Within this complex and diverse area, attention has focused on the relative timing of cleavage of the two C-N bonds, the nature of the trimethylene diradical intermediate that leads to the cyclopropane product, the stereochemistry of the reaction at each end of the three carbon fragment, the function of the residual azo group in two step mechanisms, and the role of frontier molecular orbitals [3]. Less attention has been directed toward those cases in which isomerized alkenes are formed in addition to the cyclopropane [4,5]. Such alkenes are found most frequently in cases in which there is a strongly electron-withdrawing group at a carbon that is alpha to the azo linkage. The amounts of isomerized material and their stereochemical make-up provide useful mechanistic information on the pathway to cyclopropane formation and on the role of the azo linkage.

In a synthesis of *cis*-1,2-cyclopropanedicarboxylic acid, we carried out the 1,3-dipolar cycloaddition of diazomethane to *N*-phenylmaleimide [6]. Thermolysis of the resulting 1-pyrazoline (the title compound) produced a mixture of the expected cyclopropane imide (**1**) and two isomerized, alkenic imides (**2,3**). Hydrolysis of the mixture produced *cis*-1,2-cyclopropanedicarboxylic acid (**4**), mesaconic acid (**5**) (from citraconic acid, through isomerization under hydrolysis condition [7]), and itaconic acid (**6**) (Scheme I). The relative ratios of the three imides shed new light on the mechanism of pyrazoline thermolysis.

Scheme 1



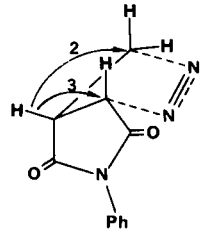

## Results and Discussion.

Reaction of an ether solution of *N*-phenylmaleimide with an ether solution of diazomethane at room temperature gave the 1,3-dipolar adduct in 80% yield. The structure of the adduct was supported by its $^1H$ and $^{13}C$ spectra. Thermolysis of this material in boiling xylene produced the three imides illustrated in Scheme I (**1-3**). The relative ratios of these three materials were 7.7/10.1/1 as determined by vpc. The relative yields after isolation by preparative tlc and column chromatography were similar.

Trapping of dipolar intermediates was attempted by carrying out the thermolysis in the presence of several 1,3-dipolarophiles: dimethyl acetylenedicarboxylate, styrene, and ethyl acrylate, in tenfold excess. The product ratios **1/2/3** with the respective addition of these materials were measured by vpc to be 8.6/12.4/1, 8.5/9.4/1, and 8.1/12.1/1. No new products were formed under these conditions.

The focus of our interest in this system is the relative ratios of the three imide products from the thermolysis of the title azo compound. The presence of alkenes is not uncommon for pyrazolines carrying an electron-withdrawing substituent on one of the carbons alpha to nitrogen. Our system differs by having the electron-withdrawing group tied back into a five-membered ring that is constrained to be nearly planar by imide resonance. Simultaneous hydrogen transfer and cleavage of both C-N bonds (a fully concerted mechanism) is unlikely in our system. During simultaneous bond reorganization, kinetic assistance would be

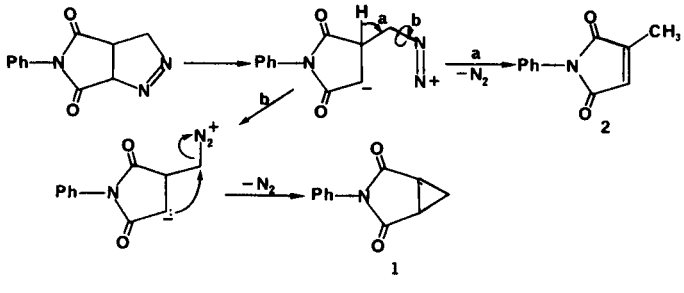
maximal when the migrating hydrogen is antiperiplanar, or nearly so, to the bond being broken, as in **7**. Migration of hydrogen in the two directions indicated by the arrows in **7** would produce the alkenes, **2** and **3**. It is not difficult to attain this arrangement in monocyclic systems, such as those studied by McGreer [4], but in the title compound the ring must buckle and form a half-chair conformation, with concomitant loss of some imide resonance, in order to attain the arrangement of **7**. Moreover, the presence of both possible rearranged alkenes requires a highly unlikely balance of bond energies in **7**.



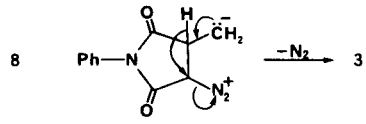
**7**

Consequently, we feel that the mechanism of decomposition of the title compound more likely follows the common two step sequence for highly unsymmetrical azo compounds [2,8]. The first bond to break would be the one located between the azo group and the electron-withdrawing group, to form a dipolar intermediate (Scheme II, first step). The cyclopropane **1** can be formed from this intermediate by rotation about the C-C bond and backside displacement by the carbanion lone pair on the remaining C-N bond (Scheme II, pathway b) [9]. The fused imide

Scheme 2



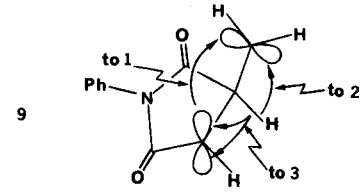
ring, however, prevents the optimal backside arrangement from occurring. The major alkene **2** may be formed by hydride shift in the dipolar intermediate (pathway a). The mechanism of Scheme II alone cannot explain all three products, as the second hydride shift product (**3**) would have to come from cleavage of the stronger C-N bond, **8**. Formation of **3** from the dipolar intermediate of Scheme II would have required a proton shift to the carbanion center (the dipolar species of opposite polarity, with positive charge adjacent to the carbonyl species, could lead to **3** but seems unlikely).



**8**

We attempted to trap the dipolar species of Scheme II with the dipolarophiles added in tenfold excess to the reaction mixture. The lack of perturbation of the reaction mixture in the presence of the dipolarophiles indicates either that the dipole is not present or that its subsequent reactions are faster than the intermolecular reaction. We also checked product stability to ensure that the hydride shift products were primary. Heating the cyclopropane imide **1** at 160° for 0.5 hour showed no isomerization to **2** or **3**.

The completely concerted mechanism appears to be excluded by geometry. The stepwise mechanism of Scheme II with the nitrogen-containing dipolar intermediate can explain the products only if a parallel mechanism is invoked that involves cleavage of the stronger C-N bond (to give **3**). Alternatively, all of the products may be explained in terms of the unencumbered trimethylene fragment produced by the stepwise cleavage of both C-N bonds. This dipolar or diradical intermediate formed after expulsion of dinitrogen would have the geometry illustrated in structure **9**. This arrangement could be obtained either by direct loss of dinitrogen with retention at both ends of the trimethylene fragment or by secondary rotation of a residual C-N bond followed by loss of dinitrogen, similar to Scheme II but without ring closure. This latter pathway would lead to inversion at the $CH_2$ center, which cannot be detected in this system.



**9**

The geometry of **9** is almost perfect for migration of the indicated hydrogen to give the major alkene **2**. Only a small rotation is needed to give the cyclopropane **1**. On the other hand, the minor alkene **3** cannot be formed readily without deforming the imide ring (again, the deformation would be toward a half-chair conformation), with disruption of imide resonance. This is the case whether the hydrogen migrates to the same or to the opposite side of the ring (both modes are shown in **9**).

Thus the unusual product distribution found in the thermolysis of the title compound can be explained in terms of orbital arrangements in a nitrogen-free trimethylene intermediate (**9**) or by two parallel pathways involving nitrogen-containing dipoles [9] (Scheme II plus **8**). The presence of both rearranged alkenes is easily explained by

**9**. The dual pathway mechanism or one involving concerted processes (**7**) requires that a significant portion of the reaction (to give **3**) occurs by initial cleavage (or more advanced bond breaking in **7**) of the stronger C-N bond.

## EXPERIMENTAL

7-Phenyl-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-dione.

An ethereal solution of *N*-phenylmaleimide was treated with an ethereal solution of diazomethane for 1 hour at room temperature. The title compound was obtained in 80% yield, mp 177-179° dec; $^1$H nmr (perdeuterioacetonitrile): δ 3.38 (t of d (J = 5.5, 8.5 Hz), 1, H5), 4.48-5.22 (m, 2, $CH_2$), 5.78 (d of t (J = 2.5, 8.5 Hz), 1, H1), 7.10-7.60 (m, 5, arom); $^{13}$C nmr (perdeuterioacetone): δ 38.73 (d, C5), 81.31 (t, C4), 95.16 (d, C1), 127.84, 129.30, 129.67, 133.18 (arom), 176.32 (s, CO), 176.32 (s, CO); ir (potassium bromide): 3000, 1720 cm$^{-1}$.

Thermolysis.

Decomposition of the title compound was complete in boiling xylene (138°) after 0.5 hour as determined by tlc (silica gel); three products were formed with $R_f$ 0.56, 0.36, and 0.32 in 9/1 chloroform/ethyl acetate or 0.44, 0.28, and 0.20 in diethyl ether. Separation of the three components was effected by preparative tlc (silica gel, 20 × 20, 2 mm, diethyl ether) on a 0.3 g scale or by column chromatography (silica gel) on a 2 g scale. The structures of the three products were proved by comparison with authentic samples [10]: *N*-phenylimide of citraconic acid (**2**): $R_f$ 0.44 (ether); mp 98-100° (chloroform/petroleum ether); $^1$H nmr (chloroform): δ 2.15 (d (J = 3 Hz), 3, $CH_3$), 6.45 (m, 1, CH), 7.40 (s, 5, arom); ms: 187 ($M^+$); *N*-phenylimide of *cis*-1,2-cyclopropanedicarboxylic acid (**1**): $R_f$ 0.20 (ether); mp 127-129° (chloroform/petroleum ether); $^1$H nmr (chloroform): δ 1.40-1.70 (m, 2, $CH_2$), 2.61 (d of d (J = 8 Hz), 2, CH), 6.97-7.55 (m, 5, arom); ms: 187 ($M^+$); *N*-phenylimide of itaconic acid (**3**): $R_f$ 0.28 (ether); mp 118-120° (chloroform/petroleum ether); $^1$H nmr (chloroform): δ 3.45 (t (J = 3 Hz), 2, $CH_2$), 5.73 (t (J = 2 Hz), 1, CH), 6.43 (t (J = 2 Hz), 1, CH), 7.20-7.40 (m, 5, arom); ms: 187 ($M^+$). After identification of the compounds, relative amounts of the components in the crude mixture could be estimated by examination of the $^1$H nmr spectrum of the mixture: **1/2/3** = 5.0/6.0/1.0. The products were analyzed by vpc on a glass column of length 2 m containing 10% silicon OV 101, with temperature programing from 70 to 290°. The components eluted in the order **2/3/1** and in the ratio 10.1/1/7.7. Injection of the starting material pyrazoline as an acetone solution led to pyrolysis on the column and gave the same three product peaks in the ratio 6.5/1/3.6. Thermolysis of the pyrazoline (0.35 mmole) in the presence of a tenfold molar excess of dimethyl acetylenedicarboxylate, styrene, or ethyl acrylate was carried out in 3 ml of xylene for 0.45 hour. The products were analyzed by vpc under the same conditions above to give the product ratios listed in the Results section. Acid hydrolysis (20% hydrochloric acid) of **1-3** gave respectively the dicarboxylic acids **4-6** (Scheme I).

*Anal.* Calcd. for $C_{11}H_9NO_2$: C, 70.57; H, 4.85; N, 7.48. Found: (**1**): C, 70.41; H, 4.70; N, 7.33; (**2**): C, 70.40; H, 4.90; N, 7.21; (**3**): 70.35; H, 4.81; N, 7.59.

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