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THE THERMAL DECOMPOSITION OF trans-3,5-DIPHENYL-1-PYRAZOLINE AND trans-3,5-BIS-(p-METHOXYPHENYL)-1-PYRAZOLINE

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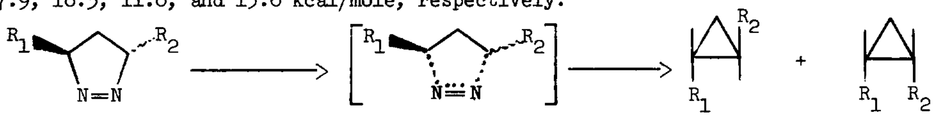
The synthesis and activation energies for the thermal decomposition of trans-3,5-diphenyl-1-pyrazoline (1a), trans-3,5-bis-(p-methoxyphenyl)-1-pyrazoline (1b), cis-3,5-bis-(p-methoxyphenyl)-1-pyrazoline (1c), and cis-3,5-bis-(p-chlorophenyl)-1-pyrazoline (1d), have been previously reported.[1,2] The activation energies were reported to be 17.9, 16.3, 11.8, and 15.6 kcal/mole, respectively.[2]



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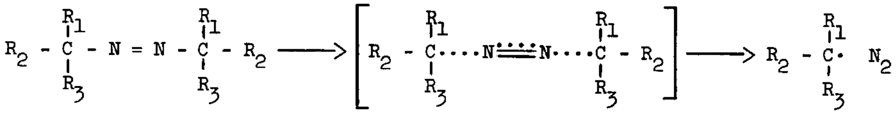
1a trans, $R_1 = R_2 = C_6H_5$
b trans, $R_1 = R_2 = p\text{-}CH_3O\text{-}C_6H_4$
c cis, $R_1 = R_2 = p\text{-}CH_3O\text{-}C_6H_4$
d trans, $R_1 = R_2 = p\text{-}Cl\text{-}C_6H_4$
e trans, $R_1 = R_2 = CH_3$
f $R_1 = R_2 = H$

The mechanism of decomposition of 1-pyrazoline (1f) and 3,5-dimethyl-1-pyrazoline (1e) has been extensively researched and the thermal mode of decomposition is thought to be a concerted two-bond cleavage (1 ⟶ 2)[3] similar to that reported for symmetrically substituted azoalkanes (5 ⟶ 6).[4,5] If 3,5-diphenyl-1-pyrazoline proceeds by the same mechanism, a value for the activation energy can be approximated from existing data. Replacing two methyl groups in 2,2'-dimethyl-2,2'-azopropane (5a) with phenyl groups to give 2,2'-diphenyl-2,2'-azopropane (5b) brings about a reduction in the activation energy from 43.1 kcal/mole[6] for 5a to 29.7 kcal/mole[5] for 5b or a ΔEa of 13.4 kcal/mole. If the same comparison in 1-pyrazolines is valid, trans-3,5-diphenyl-1-pyrazoline (1a) would be



$$R_2-\underset{R_3}{\overset{R_1}{C}}-N=N-\underset{R_3}{\overset{R_1}{C}}-R_2 \longrightarrow \left[R_2-\underset{R_3}{\overset{R_1}{C}}\cdots N\equiv N\cdots\underset{R_3}{\overset{R_1}{C}}-R_2\right] \longrightarrow R_2-\underset{R_3}{\overset{R_1}{C}}\cdot \quad N_2$$

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5a $R_1 = R_2 = R_3 = CH_3$

b $R_1 = R_2 = CH_3$, $R_3 = C_6H_5$

c $R_1 = R_2 = H$, $R_3 = CH_3$

d $R_1 = H$, $R_2 = CH_3$, $R_3 = C_6H_5$

expected to have an activation energy 13.4 kcal/mole less than the value of 40.2 kcal/mole reported for *trans*-3,5-dimethyl-1-pyrazoline[3a] (1e) or 26.8 kcal/mole. A similar value of 26.5 kcal/mole is obtained from the comparison of azoethane (5c), Ea = 48.5 kcal/mole,[7] and 1,1'-diphenyl-1,1'-azoethane (5d), Ea = 32.6 kcal/mole[8] with 1-pyrazoline (1f) Ea = 42.4 kcal/mole[3a] where the substitution change is phenyl for hydrogen.

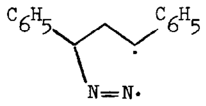
We have redetermined the rates and activation parameters for *trans*-3,5-diphenyl-1-pyrazoline (1a) and *trans*-3,5-bis-(p-methoxyphenyl)-1-pyrazoline (1b). The pyrazolines were synthesized according to the literature[1,2] but in our hands the *cis* and *trans* methoxy (1b and 1c) could not be separated. However, the *trans*-pyrazoline (1b) could be isolated after partial decomposition of a mixture of 1b and 1c. The *cis* (1c) decomposes much more rapidly and the decomposition products are readily separated from the unreacted *trans*-pyrazoline (1b). The kinetics were monitored on a constant volume variable pressure kinetic apparatus.[6] The activation parameters were calculated by a least-squares treatment of the rate data.

TABLE 1

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR DECOMPOSITION OF PYRAZOLINES

trans-3,5-Diphenyl-1-pyrazoline			*trans*-3,5-Bis-(p-methoxyphenyl)-1-pyrazoline		
Temp, °C	kx10^4, sec^{-1}	Ea*, kcal/mol	Temp, °C	kx10^4, sec^{-1}	Ea*, kcal/mol
60.0	0.78	27.5±0.5	60.2	1.08	26.1±0.6
65.0	1.41		70.0	3.97	
70.0	2.68		80.0	10.9	
75.0	4.51	Log A	85.0	17.7	Log A
80.0	7.71	14.1	90.0	29.0	14.9
83.5	12.7				
84.8	15.0				
90.0	23.5				

The results listed in Table 1 indicate that the energies of activation for both pyrazolines are close to the approximated values (26.5 and 26.8 kcal/mole), thus establishing the original work to be in error. Furthermore, these results help substantiate the concerted mechanism theory for the thermal decomposition of pyrazolines. Each phenyl group brings about the same degree of stabilization (same ΔEa) in the ring closed azo compound (pyrazoline) as in the open chain analog. This would militate against a two-step mechanism involving formation of an azo alkyl diradical intermediate (8) in the rate determining step as has been postulated to explain the stereochemistry of decomposition of exo,exo-5,6-dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene (9).[9]



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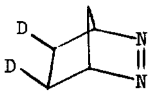

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An interesting aspect of this work is the relatively small difference in the activation parameters between the two pyrazolines. This small substituent effect parallels the results found for substituted azocumenes,[10,11] and is probably the result of a dilution effect by the phenyl group. It has been shown that substituent interactions can be quite substantial in azo compound decomposition if the demand for stabilization is large.[12]

We have also observed that the degree of stereoselectivity in ring closure to form 1,2-diphenylcyclopropane is temperature dependent. The thermal decomposition of *trans*-3,5-diphenyl-1-pyrazoline (1a) at 85° C gives a mixture of 90.8% *trans*-1,2-diphenylcyclopropane (3) and 9.2% *cis*-1,2-diphenylcyclopropane (4) while at 50° C the *trans* increases to 94.0% and the *cis* decreases to 6.0%.[*] This increase in stereoselectivity at the lower temperature appears to be a result of the competition between bond formation and bond rotation of the intermediate diradical. Further experiments are in progress to substatiate this result.

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[*] A more extensive study by C. Deboer and G. S. Hammond reveals this same stereoselective trend. We thank Dr. Deboer for communication of these results prior to publication.

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