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The Reaction between Diazoalkanes and Allylic Halides Carrying Electronegative γ-Substituents. 1. Solvent Effects in the Decomposition of 4-(1-Bromo-1-methylethyl)-4,5-dihydro-3*H*-3,3-pyrazoledicarbonitrile

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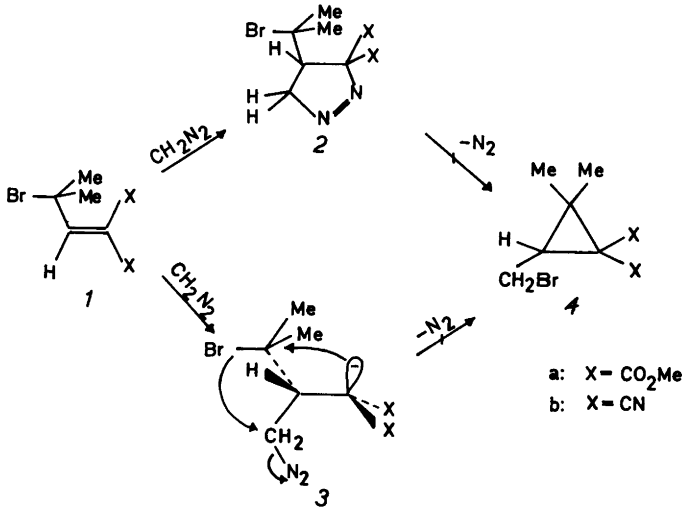
The formation of the title compound and its decomposition in several solvents is described. In nonpolar solvents both a cyclopropane and an olefinic product are formed; in polar solvents, both protic and aprotic, the cyclopropane is the only product observed. Rate of formation of the cyclopropane is very solvent dependent, while the olefin is formed at nearly the same rate in all solvents. The presence of the bromine atom in the side chain has a very great effect on the product distribution and on the rate of cyclopropane formation. Bonding in the proposed transition state is discussed.

Based on our studies on the reaction of nucleophiles with activated allylic halides to produce cyclopropanes,[1–5] further investigations involving attack on the double bond of such halides were initiated. In particular, we were interested in whether diazomethane in its reaction with the allylic bromides *1* yields the Δ^1-pyrazolines *2* and, if formed, how these compounds decompose under given conditions (Scheme 1).



Scheme 1.

0302-4369/83 $2.50

If, as generally accepted,[6] formation of pyrazolines results from a concerted 1,3-dipolar cycloaddition to the double bond of the dipolarophile, the reaction of diazomethane with the bromides *1* should give *2*. On the other hand, if a step-wise mechanism operates, as invoked in a few cases,[7,8] the carbanion being developed in the γ-position might competitively expel the bromide to form cyclopropane *4* (Scheme 1). The dipolar species *3* is conceptually similar to the one proposed in the reported cyclopropane-forming reactions.[1]

The reaction between diazomethane and bromides *1*, however, proceeded without detectable amounts of nitrogen being evolved. While *1a* reacted very slowly,[9] *1b* immediately consumed diazomethane at −15 °C with concurrent precipitation of a white product. Based on spectroscopic evidence, the products were given the Δ^1-pyrazoline structures *2a* and *2b*, respectively. The exclusive formation of pyrazolines strongly supports the simultaneous formation of the new σ-bonds in this type of cycloaddition reactions as both *1a* and *1b* react extremely fast with nucleophiles to give cyclopropanes with the assumed intermittency of carbanions similar to *3*.[1–3]

Thermolyses of Δ^1-pyrazolines analogous to *2* (*i.e.* with two electronegative 3-substituents) usually lead to mixtures of cyclopropanes and olefins.[10–11] The stereochemical outcome of such decompositions has received quite some attention,[10] and we will deal with these problems in forthcoming papers. With symmetrical substitution at the 3- and 5-positions, respectively, this problem is eliminated in our Δ^1-pyrazolines.

The thermal decomposition of *2a* to a Δ^2-pyrazolinium bromide is described earlier.[9]

In contrast to *2a*, the cyano analogue, *2b*, is very unstable. In dry condition it decomposes rapidly after a few minutes even at −35 °C with considerable smoke formation leaving only traces of unidentified materials behind. In solution, however, it decomposes controllably with nitrogen evolution to mixtures of cyclopropane *5* and alkene *6*; the structure of the latter compound easily verified spectroscopically. The assignment of structure *5* (and not the theoretically possible structure *4*) to the decomposition product was based on ^{13}C NMR where the carbon atom carrying the bromide atom was quarternary and on the C–H stretching vibrations in the IR-spectrum (see Experimental).

As seen from Table 1, the product composition shows a strong solvent dependency. In nonpolar aprotic solvents alkene *6* is dominating while in polar solvents, both protic and aprotic, cyclopropane *5* is formed almost exclusively.

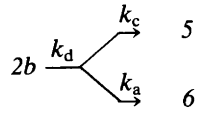
Table 1. Product distribution in the decomposition of Δ^1-pyrazoline *2b*.[a]

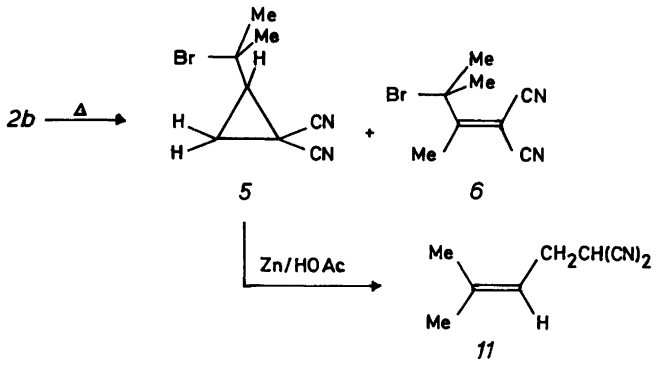
Solvent	*t* (°C)	*5*	*6*
C_5H_{12}	25.0	31	69
C_6H_6	27.3	13	87
	17.6	15	85
Et_2O	25.0	9	91
$CHCl_3$	25.0	20	80
	17.6	22	78
	6.7	25	75
	−5.5	30	70
	−16.2	40	60
CH_2Cl_2	25.0	28	72
$(CH_2Cl)_2$	27.2	31	69
	22.3	32	68
	10.8	40	60
	−10.4	57	43
Bu^iOH	−19.3	100	0
	−37.7	100	0
C_5H_5N	−9.5	100	0
	−40.1	100	0
Pr^iOH	−16.0	100	0
	−38.0	100	0
$(CH_3)_2CO$	25.0	85	15
	−19.3	100	0
	−43.4	100	0
EtOH	−25.0	100	0
	−55.2	100	0
MeOH	25.0	100	0
	−29.0	100	0

[a] Yields in percent.

The decomposition reaction was followed kinetically in several solvents at different temperatures by measuring the evolution of nitrogen. The decomposition of pyrazoline *2b* was strictly first order in all solvents and at all temperatures with correlation coefficients ranging from 0.989 to 1.000 (Table 2).

It thus seems reasonable to assume that the decomposition of *2b* consists of two competitive reactions each of first order in the pyrazoline:





Scheme 2.

Thus, $k_d=k_c+k_a$, where k_d is the rate constant for decomposition of *2b* and k_c and k_a are the rate constants for formation of cyclopropane *5* and alkene *6*, respectively. It can be shown that

$$k_c=k_d\cdot(5)_\infty/[(5)_\infty + (6)_\infty]$$

and

$$k_a=k_d\cdot(6)_\infty/[(5)_\infty + (6)_\infty]$$

Table 2. Experimental kinetic data for the decomposition of *2b* and calculated rate constants for formation of *5* and *6*.[a]

Solvent	t (°C)	$k_d\cdot10^5$	$k_a\cdot10^5$	$k_c\cdot10^5$	r^b
C_6H_6	27.3	553.0	482.0	71.0	1.000
	17.6	176.0	149.0	27.0	0.999
$CHCl_3$	17.6	251.0	196.0	55.0	0.999
	6.7	69.5	52.4	17.1	0.999
	−5.5	16.0	11.2	4.8	0.997
	−16.2	3.6	2.2	1.4	0.999
$(CH_2Cl)_2$	27.2	498.0	333.0	165.0	0.999
	22.3	330.0	223.0	107.0	0.998
	10.8	104.0	62.5	41.2	1.000
	−10.4	10.7	4.5	6.2	0.998
Bu^iOH	−19.3	225.0	0	225.0	0.999
	−29.7	64.4	0	64.4	1.000
	−37.7	14.3	0	14.3	0.999
C_5H_5N	−9.5	275.0	0	275.0	1.000
	−18.6	159.0	0	159.0	0.998
	−40.1	44.0	0	44.0	1.000
Pr^iOH	−16.0	680.0	0	680.0	0.988
	−29.0	112.0	0	112.0	0.989
	−38.0	28.0	0	28.0	0.998
$(CH_3)_2CO$	−19.3	324.0	0	324.0	0.992
	−28.3	169.0	0	169.0	0.997
	−43.3	51.2	0	51.2	0.996
EtOH	−25.0	815.0	0	815.0	0.990
	−29.0	405.0	0	405.0	0.999
	−49.1	55.0	0	55.0	0.995
	−55.2	11.0	0	11.0	0.995

[a] Unit for rate constants: sec^{-1}. [b] Correlation coefficients for first order plot.

Table 3. Activation parameters for the decomposition of Δ^1-pyrazoline *2b* at 244.2 K.[a]

Solvent	C_6H_6	$CHCl_3$	$(CH_2Cl)_2$	Bu^{t}OH	C_5H_5N	Pr^{i}OH	$(CH_3)_2C{=}O$	EtOH
$E_T(30)$[b]	144.3	163.5	175.2	204.9	168.1	203.2	176.5	217.0
Cyclopropane (*5*) formation								
$k_c \cdot 10^6$	0.86	2.6	5.0	589	882	1120	1620	4810
$\Delta G^{\neq}$	87.8±0.8	86.1±0.8	83.6±0.8	74.9±0.8	74.0±0.8	73.6±0.8	72.8±0.8	70.3±0.8
$\Delta H^{\neq}$	70.7±7.5	65.7±1.7	55.6±1.7	72.8±1.7	28.9±0.8	71.1±1.3	35.5±1.3	56.9±0.8
$\Delta S^{\neq}$	−70.6±26.3	−83.2±7.5	−114.2±7.1	−8.8±7.1	−185.3±4.6	−9.6±5.9	−152.2±5.4	−55.6±4.2
r[c]	– [d]	1.000	1.000	0.997	1.000	1.000	1.000	0.987
Alkene (*6*) formation								
$k_a \cdot 10^6$	1.4	2.9	3.1	(6.5)	(2.3)	(6.5)	(2.9)	(9.9)
$\Delta G^{\neq}$	86.9±0.8	85.7±0.8	85.3±0.8	(83.6)	(85.7)	(83.6)	(85.3)	(82.8)
$\Delta H^{\neq}$	86.1±7.5	80.7±1.7	74.4±1.7					
$\Delta S^{\neq}$	−3.3±5.4	−20.1±7.5	−44.7±7.1					
r[c]	– [d]	1.000	1.000					

[a] Units are kJ mol^{-1} for $\Delta G^{\neq}$ and $\Delta H^{\neq}$, J mol^{-1}K^{-1} for $\Delta S^{\neq}$. Extrapolated values in brackets. Limit of errors, see Experimental. [b] Solvent polarity parameters (kJ mol^{-1}) from Ref. 13. [c] Correlation coefficients for Arrhenius plots. [d] Only two temperatures.

where $(5)_\infty$ and $(6)_\infty$ represent the final concentrations of *5* and *6*.[12] Thus, by measuring the decomposition rate of *2b* and establishing the final product composition the individual rate constants k_a and k_c can be calculated.*

Table 2 gives the measured rates of decomposition of *2d* and the calculated rates of formation of *5* and *6*. Table 3 gives the relative rates of formation of *5* and *6* and the activation parameters as obtained from the Arrhenius-plots and the Gibbs-Helmholtz equation.

A striking feature from Table 3 is the very strong rate acceleration in the cyclopropane formation with increasing solvent polarity, an observation pointing to a transition state more polar than the ground state.

Several empirical parameters have from time to time been used to relate reaction rates or equilibria positions to solvent polarity.[13] The list of $E_T(30)$-values, obtained from the solvent-dependent transition-energies in the absorption spectra of pyridinum-N-phenoxide betaines, is probably the most comprehensive solvent scale to date and exhibits good linear correlation with kinetic data.[14] Fig. 1 relates the free activation energies for cyclopropane formation to $E_T(30)$. Except for the solvents pyridine and acetone a fairly good linear relationship is obtained (correlation coefficient 0.980). The 10^2-fold rate enhancement in pyridine and acetone (as calculated from the $\Delta G^{\neq}$ *vs.* $E_T(30)$ plot) is also reflected in the extremely low activation enthalpies (Table 3). These low values and the large negative activation entropies indicate a highly solvated transition state. It has been proposed that the decomposition of 1-pyrazolines with electronegative 3-substituents starts with heterolytic cleavage of the N2—C3 bond to form a zwitterion.[10] The carbanionic part is internally stabilized by the 3-substituents. This is demonstrated by a reduction in $\Delta G^{\neq}$ of 25–35 kJ/mol in the decomposition of the nonbrominated analogues of *2* when the two methoxycarbonyl groups at C3 were replaced with cyano groups.[10] In this connection it is interesting to note that while pK_A is two units lower for malononitrile than for dimethyl malonate (thermodynamic acidity), the rate of ionization (kinetic acidity) is

* Cyclopropane *5* decomposes in the gas chromatograph and therefore the product composition was estimated by ^{1}H NMR (see Experimental).

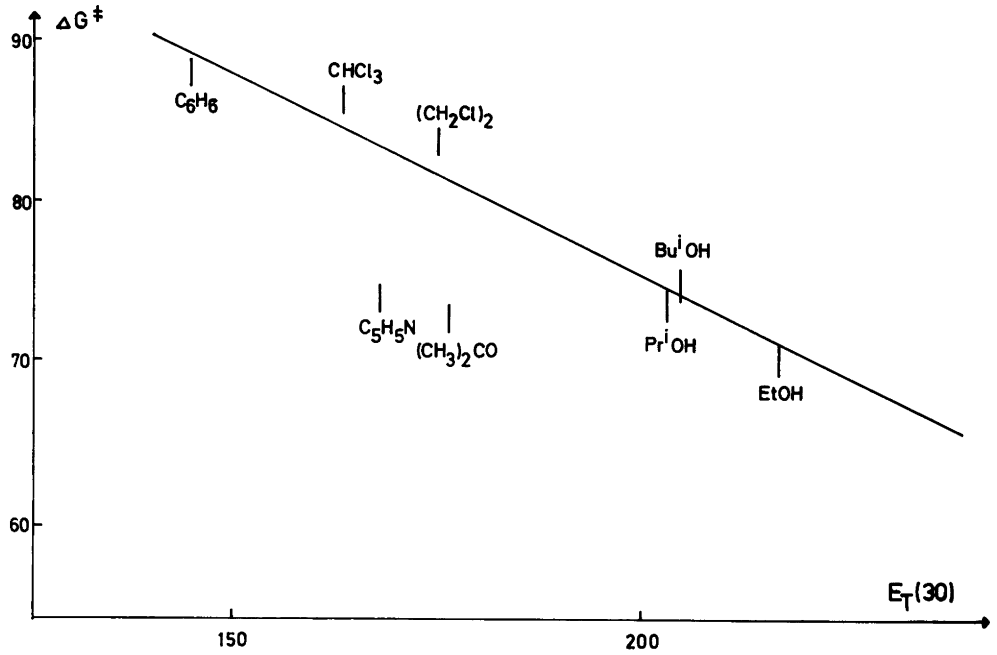


Fig. 1. Plot of the free activation energy *vs.* the solvent polarity parameter $E_T(30)$. Units kJ mol^{-1}. Least square line $\Delta G^{\neq} = -3.76\ E_T(30) + 482.9$ (r=0.980).

about 6×10^2 higher for the former compound.[15] The effect of changing the 3-substituents in our studies is a complete change in product formation. While *2b* undergoes ring cleavage, *2a* forms quantitatively a 2-pyrazoline as demonstrated in an earlier paper.[9]

The electron pair donation capacity (EPD) of pyridine as measured by the donation number (DN) * is higher than for ethanol, *i.e.* pyridine is a very good cation solvator. Acetone is also a good cation solvator, being an n-donor[17] or a coordinating solvent.[18]

A second feature from Table 3 is the relatively high activation enthalpies coupled with small entropy changes in the protic solvents. In contrast to the situation in aprotic solvents it looks as if solvation of the transition state (causing lowering of the activation entropy) is less important, obviously an erroneous conclusion. The reason for this observation must be sought in the structure of protic solvent where the molecules are held together by hydrogen bonds. By introducing charged particles (read: the charged transition state) into the solvent, energy is required to break these bonds (increasing $\Delta H^{\neq}$-term) and more degrees of freedom given to the solvent molecules (increasing $\Delta S^{\neq}$-term). As pointed out earlier, the negative part of the zwitterion from *2b* is internally stabilized, thus the unique capacity of protic solvents to solvate anions through hydrogen bondings is less demanded. The electron pair donation capacity of ethanol as measured by its donation number (*vide supra*) is lower than for pyridine making it an average cation solvator.[16] To conclude, the macroscopically measured activation enthalpies and entropies must both be higher in protic solvents since rupture of the solvent structure is involved.

In many reactions $\Delta H^{\neq}$ is linearly related to $\Delta S^{\neq}$.[19] Fig 2 represents such a plot where the line for the protic solvents (correlation factor 0.997) is almost parallel and lower than for the aprotic solvents (correlation factor 0.992). A similar "double line" plot is also found for the decomposition of triethylsulfonium bromide,[19,20] where the line for the protic solvent is higher than for the aprotic solvents. This is certainly expected

* Defined as the negative ΔH values for 1:1 adduct formation between antimon pentachloride and electron pair donor solvents.[16]

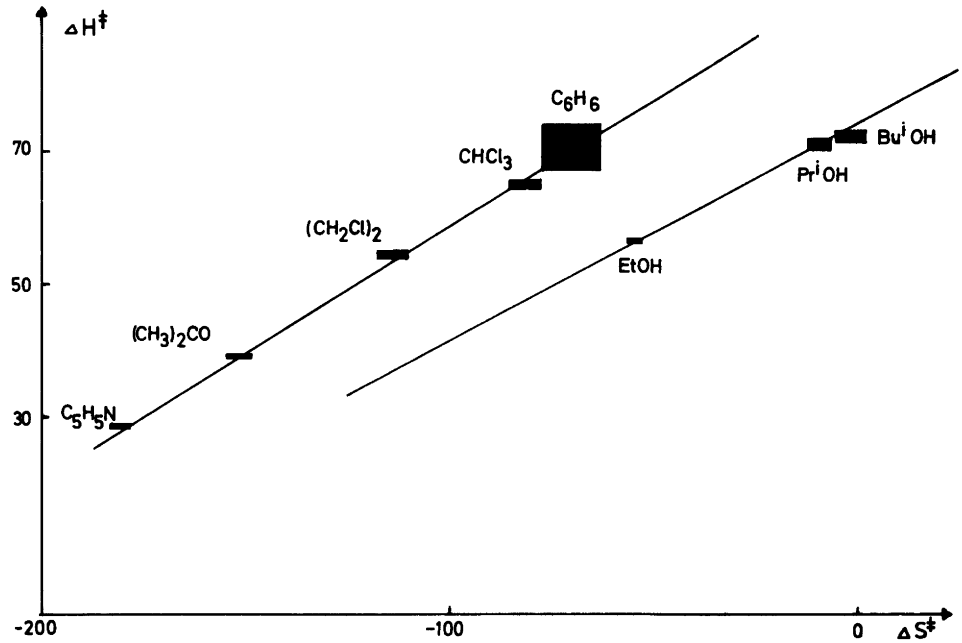
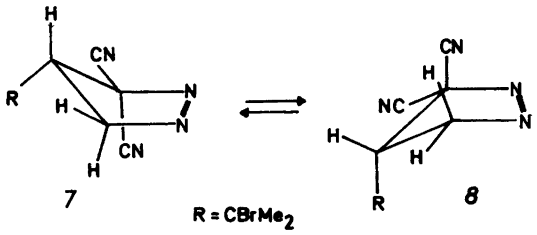


Fig. 2. Plot of activation enthalpy *vs.* activation entropy. Units for enthalpy kJ mol^{-1}, entropy J mol^{-1} K^{-1}. The black rectangles represent the maximum error along both axes. Least square lines:
Upper: $\Delta H^{\ddagger}=0.382\Delta S^{\ddagger}+97.5$ ($r=0.992$).
Lower: $\Delta H^{\ddagger}=0.324\Delta S^{\ddagger}+74.9$ ($r=0.997$).

since charge is dispersed in the transition state as reflected in the rate decrease with increasing polarity of the solvents. Fully aware of the danger in drawing physical conclusions based on such interrelationship of thermodynamic parameters,[19,21] it is nevertheless interesting to note that the difference in the intercept for these lines is 16–25 kJ/mol in the enthalpies which is of same order of magnitude as the strength of the hydrogen bond in alcohols (ethanol: 26 kJ/mol[22]).

Alkene formation is not observed, neither in the protic solvents nor in the polar aprotic solvents (pyridine, acetone) at low temperature (Table 1). Based on a linearity of the free activation energy *vs.* the $E_T(30)$ values for benzene, chloroform and 1,2-dichloroethane (correlation factor 0.990), extrapolated values for $\Delta G^{\ddagger}$ (and k_a) are given in brackets in Table 3 for the polar aprotic and protic solvents. These calculated $\Delta G^{\ddagger}$-values seem to be of the right order of magnitude, *i.e.* 8–12 kJ/mol higher than the $\Delta G^{\ddagger}$-values for cyclopropane formation (corresponding to 10^2–10^3 difference in the rate constants) as no alkenes were observed in these solvents. The relatively low solvent dependence in the alkene formation thus observed indicates a transition state having a comparatively small charge separation.

The effect of having a bromine atom in the side chain in the 4-position of *2b* is rather dramatic. The rate of decomposition is about 50-fold higher than that of the nonbrominated analogue,[10] and the product ratio (alkene–cyclopropane) is changed from 84:16 to 0:100 at 244.2 °K (Table 4). This accelerated decomposition rate is reflected in a 325-fold rate *increase* in cyclopropane formation and an 8-fold rate *decrease* in alkene formation. The latter decrease is probably caused by steric compression in the transition state. It is established by X-ray crystallography that Δ^1-pyrazolines exhibit C_s-symmetry in the solid phase,[23] with C4 at the flip of the envelope, the plane through C3–C4–C5 forming angles of 20–30° to the plane through C3–N2–N1–C5. In solutions conformational equilibrium between *7* and *8* is suggested (Scheme 3).[24]

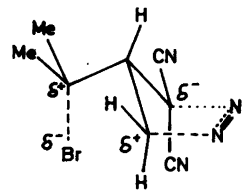


Scheme 3.

Analogous to cyclohexane systems, large groups in five-membered rings with C_s-symmetry will tend to prefer pseudoequatorial positions, thus it is highly likely that for *2b* the equilibrium *7*⇌*8* is more displaced to left than for the non-brominated analogue. For stereoelectronic reasons, alkene *6* most likely is formed from conformer *8* where overlap between the σ-electrons of the C–H bond at C4 and the back-lobe of the C5–N1 sp^3-orbital can take place.

The large increase ($\Delta\Delta G^{\neq}$~12 kJ mol^{-1}) in the rate of cyclopropane formation for *2b* as compared to its non-brominated analogue is more difficult to explain. As demonstrated above, the transition state for cyclopropane formation is highly polarized, hence any polarizable element in the molecule will tend to lower the free activation energy. A closer look at models of conformer *7* discloses that the bromine atom in *2b* may take positions close to C5.* In the transition state for cyclopropane formation some positive charge is built up at C5, as will be demonstrated in a forthcoming paper.[25] Thus dipole–dipole interactive stabilization of the transition state as indicated in *9* may facilitate cyclopropane formation from *2b* as compared to its nonbrominated analogue.

As mentioned above, the large solvent effects observed for cyclopropane formation point to a polarized transition state. In accordance with the fact that the stereochemistry is retained in the cyclopropane formation,[23c] it is assumed that the N2–C3 bond is not completely broken before bonding between C3 and C5 has started, and a transition state like *10* is proposed.



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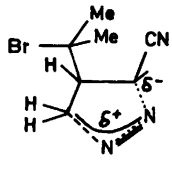

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It may be argued that there is a possibility that the N2–C3 bond may be completely broken and that rotation around the C4–C5 bond is slower than C3–C5 bond formation and thus explaining the retained stereochemistry. Against this argument stands the very low rotation barrier in C–C single bonds with low substitution on the carbon atoms involved. The C5–N1 bond is probably only partially broken in the transition state. This is indicated by the low reaction constant found for 5-aryl substituted 1-pyrazolines.[25]

Table 4. Comparison of rate constants and activation parameters for the decomposition of *2b* and its nonbrominated analogue [a] in ethanol at 244.2 K.[b].

	2b	Non-brominated *2b*
Cyclopropane formation		
$k_c \cdot 10^6$	4810	14.8
$\Delta G^{\neq}$	70.3±0.8	82.0±0.4
$\Delta H^{\neq}$	56.9±0.8	74.0±0.8
$\Delta S^{\neq}$	−55.6±4.2	−32.2±4.2
r^c	0.987	1.000
Alkene formation		
$k_c \cdot 10^6$	(9.9)	77.3
$\Delta G^{\neq}$	(82.8)	78.2±0.4

[a] Calculated from the kinetic data in Ref. 10. [b] Units are kJ mol^{-1} for $\Delta G^{\neq}$ and $\Delta H^{\neq}$, J mol^{-1}K^{-1} for $\Delta S^{\neq}$. Extrapolation data in parentheses. Limit of error, see Experimental. [c] Correlation coefficients for Arrhenius plot.

EXPERIMENTAL

General. Melting points (uncorrected) were determined on a micro hot-stage. IR spectra were recorded on a Perkin-Elmer 457 Grating Infrared spectrophotometer, ^{1}H NMR spectra on a Varian HA 100-15D spectrometer operating at 98 MHz, ^{13}C NMR spectra on a JEOL FX-60 FT NMR

* In fact, in the crystal phase of the 5-phenyl substituted analogue of *2b*, the distance between C5 and the bromide atom is somewhat lower than the sum of their van der Vaal's radii.[23c]

spectrometer and mass spectra on an AEI MS 902 instrument. Elemental analyses were performed by I. Beetz, West Germany.

4-(1-Bromo-1-methylethyl)-4,5-dihydro-3H-3,3-pyrazoldicarbonitrile (2b). To a solution of 2-bromo-2-methylpropylidenemalononitrile (10 mmol) in diethyl ether (30 ml) was added diazomethane (11 mmol) in diethyl ether (25 ml) at −15 °C. During the addition of diazomethane *2b* precipitated as colourless needles. Decomposes rapidly in dry condition at or well below room temperature. ^{1}H NMR (acetone-d_6 at −70 °C): δ 1.99 (1H,s), 2.11 (3H,s), ABX-system: υ_A 5.71, υ_B 5.37, υ_X 3.62, J_{AX}=8.0 Hz, J_{BX}=9.0 Hz, J_{AB}=19.0 Hz.

2-(1-Bromo-1-methylethyl)-1,1-cyclopropanedicarbonitrile (5). Freshly made *2b* was decomposed in methanol at 25 °C to yield *5* as the sole product. M.P. 69–70 °C (ether–pentane). Anal. $C_8H_9N_2Br$: C, H, N. ^{1}H NMR ($CDCl_3$): δ 1.93 (3H,s), 1.96 (3H,s), A_2B-system: υ_A 2.08, υ_B 2.43, J_{AB}=9.2 Hz. ^{13}C NMR ($CDCl_3$): δ 4.3 (C1), 23.2 (C3), 32.3+32.7 (2×Me), 42.6 (C2), 57.9 (*C*-Br), 112.9+115.0 (2×C=N). IR (KBr) 3090 (m), 3010 (m) and 2980 (m) cm^{-1}.

2-Bromo-1,2-dimethylpropylidenemalononitrile (6). Freshly made *2b* was decomposed in diethyl ether at 25 °C to give an oil consisting of 9 % *5* and 91 % *6*. Upon distillation *6* was obtained in pure state. B.p. 81–83 °C/0.07 mmHg. ^{1}H NMR ($CDCl_3$): δ 2.17 (6H,s), 2.50 (3H,s).

4-Methyl-3-pentene-1,1-dicarbonitrile (11). Cyclopropane (*5*) (13 mmol) was dissolved in acetic acid (25 ml) containing a few drops of water. Zn (2 g) was added and the mixture stirred overnight at room temperature. After dilution with water, extraction with pentane gave *11* (63 %) B.p. 43–44 °C/0.05 mm Hg. Anal. $C_8H_{10}N_2$: C, H. ^{1}H NMR (CCl_4-double resonance expts): δ 1.75 (3H,d, J=1.0 Hz), 1.84 (3H,d, J=0.9 Hz), 2.68 (2H,2d, J=6.9 Hz and J=7.4 Hz), 3.64 (1H,t, J=6.9 Hz), 5.20 (1H, triplet (J=7.4 Hz) of multiplets (J=1.0 Hz)).

Decomposition of 2b. Immediately after its preparation, samples (0.5 g) of *2b* were dissolved in different solvents (50 ml) and stirred at room temperature (25.0 °C) until nitrogen evolution had ceased. After an additional hour, solvents were evaporated and the residue subjected to NMR-analyses (Table 1).

Kinetic measurements. Solvents (250 ml) were temperature equilibrated and saturated with highly purified nitrogen before samples of *2b* (0.5–1.0 g) were added. Evolved nitrogen was measured with a gas burette. Rate constants were obtained from the slope of the plot of log (v_∞–v) against time (s^{-1}). Least square treatment of the parameters gave correlation coefficients ranging from 0.989–1.000 (Table 2). Measurements were carried out for three to four halflives (*i.e.* 85–90 % completion) and the solution left at ambient temperatures for seven halflives (>97 % reaction). Solvents were evaporated and the residue subjected to ^{1}H NMR analysis to determine the ratio *5*:*6* using the integrals of the *gem.* dimethyl group as measures. Five integral traces were run for each experiment and the average values (stand. dev. <1 %) used in the calculation of rate constant for alkene (k_a) and cyclopropane (k_c) formation (Table 2). The error limits for the activation parameters entered in Table 3 are the *maximum* calculated errors [27] based on estimated error in the rate constant of 5 % whenever the rate constant k_a and k_c had to be calculated (*i.e.* when both *5* and *6* were formed) and 3 % when only cyclopropane was formed.

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