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The Reaction between Diazoalkanes and Allylic Halides Carrying Electronegative γ-Substituents. 2. Formation and Decomposition of Dimethyl 4-(1-Bromo-1-methylethyl)-5-aryl-4,5-dihydro-3*H*-3,3-pyrazoledicarboxylates

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The title compounds were synthesized by the reaction of the proper *para*-substituted phenyldiazomethanes and dimethyl 2-bromo-2-methylpropylidene-malonates. *p*-Cyano- and *p*-nitrophenyldiazomethane did not give 1-pyrazolines, but decomposed at the reaction conditions. Upon thermolyses in various solvents only cyclopropanes were obtained. Only small solvent effects were observed. The kinetic data gave good linear correlation with σ^+-data, with a reaction constant, $\rho = -1.00$.

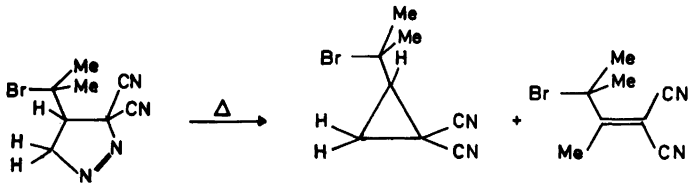
In the preceding paper of this series the decomposition of 4-(1-bromo-1-methylethyl)-4,5-dihydro-3*H*-3,3-pyrazoledicarbonitrile (*1*) was found to give cyclopropane *2* and alkene *3* (Scheme 1).[1] Formation of the former compound was shown to be strongly solvent dependent.

The transition state leading to the cyclopropane was suggested to have a considerable dipolar character with the positive end near C5. A well-known probe of charge build-up or destroying is the introduction of *p*- or *m*-substituted phenyl groups at such centers and to study rate influences exerted by these substituents, *i.e.* to test if a Hammett-type linear free energy relationship exists.[2]

5-Arylsubstituted 1-pyrazolines *6* were synthesized by reactions of the properly substituted diazomethanes (*4*) with the activated olefins *5* (Scheme 2). Unfortunately, 4-cyano- and 4-nitrophenyldiazomethanes did not react at all; after five days the diazo compounds had decomposed, leaving the olefin unreacted.

Only one of the possible stereoisomers of pyrazolines *6* was observed and the structure of *6b* was firmly established by X-ray crystallography to have *trans* configuration at the C4–C5 bond.[3] ^{1}H NMR spectra indicated analogous structures for *6a* and *6c-h*.

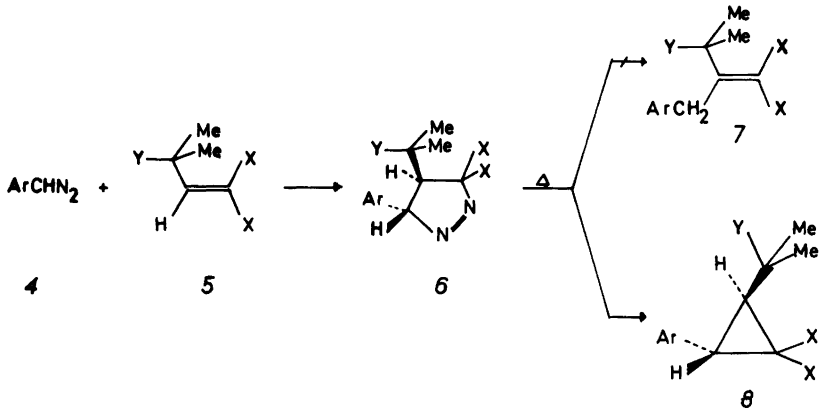
The introduction of 5-aryl substituents in the 1-pyrazolines had a great influence on their



1 2 3

Scheme 1.

0302-4369/83 $2.50



4 5 6

Scheme 2.

5a Y=Br, X=CN
5b Y=Br, X=CO_2Me
5c Y=Cl, X=CO_2Me
5d Y=H, X=CO_2Me

6a Ar=Ph, Y=Br, X=CN
6b Ar=Ph, Y=Br, X=CO_2Me
6c Ar=4-MeO–Ph, Y=Br, X=CO_2Me
6d Ar=4-Me–Ph, Y=Br, X=CO_2Me
6e Ar=4-Cl–Ph, Y=Br, X=CO_2Me
6f Ar=4-Br–Ph, Y=Br, X=CO_2Me
6g Ar=Ph, Y=Cl, X=CO_2Me
6h Ar=Ph, Y=H, X=CO_2Me

Table 1. Kinetic data for the decomposition of pyrazolines *6*.[a].

Compound	Solvent	*t* (°C)	10^4k	*r*[b]
6b	Toluene	43.0	1.5±0.1	0.991–0.997
		57.0	8.0±0.1	0.999
		72.0	54.0±3.0	0.997–0.999
	Chlorobenzene	43.0	1.2±0.1	0.990–0.999
		57.0	8.4±0.2	0.996–0.999
		72.0	53.0±2.0	0.998–0.999
	Cyclohexanone	43.0	0.9±0.1	0.991–0.997
		57.0	5.1±0.1	0.992–0.995
		72.0	31.0±2.0	0.995–0.998
	Butanol	43.0	2.0±0.1	0.998–0.999
		57.0	12.9±0.9	0.996–0.997
		72.0	84.0±4.0	0.987–0.998
6c	Toluene	31.0	2.9±0.1	0.993–0.999
		57.0	57.0±5.0	0.994–0.996
6d	Toluene	46.0	5.4±0.3	0.999
		57.0	21.5±0.1	0.999
6e	Toluene	57.0	7.1±0.4	0.998–0.999
		70.0	32.0±1.0	0.995–0.999
	Butanol	72.0	98.0±5.0	0.994–0.996
6f	Toluene	57.0	5.9±0.6	0.995–0.999
6g	Toluene	57.0	6.5±0.1	0.993–0.995

[a] Units for rate constants: s^{-1}. [b] Correlation coefficients span for first order plot; single entry means that the parallel runs had same *r*.

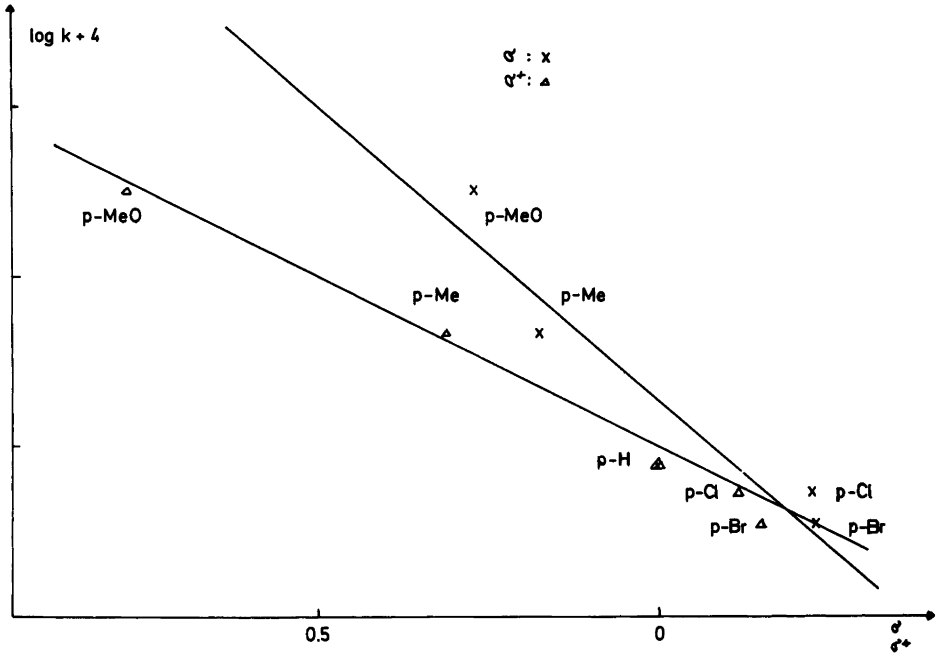


Fig. 1. Correlation of log k with σ and σ^+. Least square lines:
σ: log k= $-1.68\sigma-2.86$ (r=0.934)
σ^+: log k= $-1.00\sigma^+-3.02$ (r=0.998).

stability. Thus any attempt to isolate *6a* was in vain, it decomposes immediately to cyclopropane *8a*. However, at –70 °C it was possible to obtain its ^{1}H NMR spectrum.[4] Therefore we had to concentrate our decomposition studies on compounds with ester groups at C3 (*6b–h*).

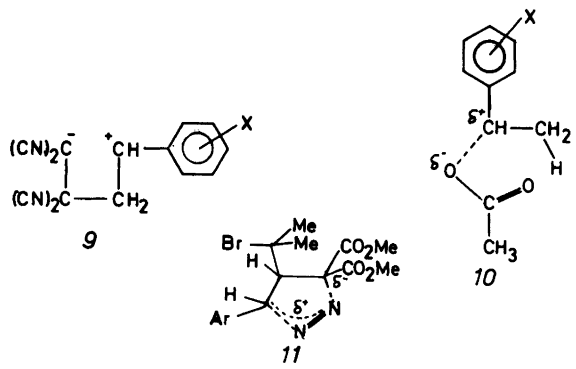
Decomposition of *6b-f* in various solvents at different temperatures gave only cyclopropane *8*, while *6g* gave small amounts of some unidentified material in addition to *8g*. *6h* gave a mixture consisting of 45 % *8h* and 55 % of an olefinic arising from isopropyl group migration from C4 to C5 during decomposition.

The decomposition reaction was followed kinetically in four solvents of different polarities, with $E_T(30)$ ranging from 141.8 to 210.0 kJ mol^{-1}.[5] The kinetics were found to be strictly first order with correlation coefficients ranging from 0.987 to 0.999 (Table 1).

In contrast to the decomposition of *1*,[1] the observed solvent dependence of the decomposition rate of *6b* was very small. Thus, while the decomposition rate of *1* increased by a factor of 1300 when going from benzene to isopropylalcohol ($\Delta E_T(30)$~60 kJ mol^{-1}), the decomposition rate for *6b* increased only by a factor of 2.5 from toluene to butanol ($\Delta E_T(30)$~70 kJ mol^{-1}).

The effect of changing the substituents in *para* position of the phenyl group is larger than the solvent effect. Thus the rate of decomposition is about 10-fold higher for *p*-MeO than for *p*-Br. With the limited number of substituents available, Fig. 1 seems to indicate that the correlation with σ^+ is better than with σ.

The correlation with σ^+ together with the negative reaction constant supports the earlier assumption that some positive charge is developing at C5 in the transition state. The rather low value of the reaction constant (ρ= –1.00) indicates that the C5–N1 bond is not completely broken. In comparison, in the S_N1 hydrolyses of substituted cumyl chlorides in 90 % aqueous acetone the reaction constant was estimated to –4.54,[6] and in the reaction of substituted styrenes with tetracyanoethylene a reaction constant of –7.1 was found, indicating a zwitterionic transi-



Scheme 3.

tion state, *9*,[7]

On the other hand, in the thermolysis of substituted 1-methylbenzylacetates a ρ-value of –0.66 was found, indicating a transition state with smaller charge separation, like *10*.[8] The reaction constant observed by us thus indicates a transition state with charge separation as shown in *11*.

As mentioned above, the introduction of a phenyl group in 5-position had great influence on the reaction rate. It changes the decomposition route too, as the 1-pyrazolinediester without 5-substituents rearranges to the corresponding 2-pyrazoline on heating.[9]

The effect of having a bromine atom in the side chain is reflected in a higher yield of cyclopropanes compared to alkenes (Table 2), which also was observed in the dicyanopyrazolines.[1,10]

The alkene formed in the decomposition of *6h* is a result of isopropyl group migration from C4 to C5. This is expected if the conformer with the migrating group pseudoequatorial is the more stable one.[11] We have found (*vide supra*) that in *6b* the phenyl and the bromoisopropyl groups take pseudoequatorial positions in the crystal phase.[3] Further, our studies on the conformations of 4,5-*trans*-disubstituted 1-pyrazolines have shown that an *increase* of the size of the 4- *and* 5-substituents tends to make the conformers with these substituents pseudo-*axial* more stable.[4] Thus, by *reducing* the size of the 4-substituent (bromoisopropyl→isopropyl) one would expect it to prefer a pseudoequatorial position, capable of migrating to the 5-position.

Contrary to the dicyanopyrazolines,[1,10] the rate of decomposition of the aryl-substituted diesterpyrazolines is much faster (approx. 12 times) *without* bromine in the side chain. Dissecting this rate into rates of formation of cyclopro-

Table 2. Rates and product distribution in the decomposition of pyrazolines *6b* and *6h* at 330.2 K.

	6b	*6h*
Rate of decomposition	$8.8.\times10^{-4}$	108.0×10^{-4}
Cyclopropane		
Yield (%)	100	45
Rate of formation	8.8×10^{-4}	50×10^{-4}
Alkene		
Yield (%)	0	55
Rate of formation	$<8.8\times10^{-6}$ [a]	58×10^{-4}

[a] Max. value as no alkene was observed.

pane and alkene, respectively, as shown before,[1] one finds that cyclopropane formation is approximately 6 times faster from the nonbrominated compound while alkene is formed more than 60 times faster from the same 1-pyrazoline (Table 2). The latter result is probably best explained by an assumed lower migratory aptitude of the bromoisopropyl group.

In the dicyanopyrazolines cyclopropane formation was approx. 325 times faster for the side-chain brominated 1-pyrazolines.[1,10] This was mainly attributed to the polarization of the C–Br bond thereby stabilizing the partly positive charge at C5 in the transition state. Such stabilizing effects from the C–Br dipole is less important in the present 1-pyrazolines since the aryl group at C5 acts as an "electron reservoir".

Likewise, the observed lack of solvent effect (*vide supra*) may be explained by intramolecular stabilization of the partly positive charge at C5 exerted by the aryl group.

EXPERIMENTAL

General. Melting points (uncorrected) were determined on a micro hot-stage. IR spectra were recorded on a JASCO IRA-1 spectrophotometer, ^{1}H NMR spectra on a Varian HA 100-15D spectrometer operating at 98 MHz, ^{13}C NMR spectra on a JEOL FX60 FT spectrometer and mass spectra on an AEI MS 902 instrument. Elemental analyses were performed by Ilse Beetz, West Germany.

Materials. The following substituted diazomethanes were synthesized according to standard literature procedures: Phenyl-,[11] 4-methoxyphenyl-,[12] 4-methylphenyl-,[11] 4-chloro- and 4-bromophenyl-,[11] 4-cyanophenyl- and 4-nitrophenyl-.[13]

*Reaction between 2-bromo-2-methylpropylidenemalononitrile (*5a*) and phenyldiazomethane (*4a*). Synthesis of 2-(1-bromo-1-methylethyl)-3-phenyl-1,1-cyclopropanedicarbonitrile (*8a*).* To *5a* (0.5 g, 2.5 mmol) in ether (10 ml) was added the red-colored solution *4a* (0.3 g, 2.5 mmol) in pentane (20 ml). Rapid decoloration with gas evolution took place within seconds and after cooling to –20 °C colorless crystals of *8a* appeared. Yield 78 %. M.p. 58–59 °C (ether–pentane). Found: C 58.6, H 4.8, N 9.8. Calc. for $C_{14}H_{13}BrN_2$: C 58.1, H 4.5, N 9.8. ^{1}H NMR (CCl_4): δ 7.37 (5H,s), 3.42 and 2.82 (2H, 2d. AB-system, J=9.0 Hz), 2.05 (3H,s), 1.95 (3H,s). IR(KBr): 2240 (m), 1380 and 1400 (s) cm^{-1}. MS: m/e 287–289 (M^+), 209 (M–Br). When the reaction was carried out at –78 °C, ^{1}H NMR signals were obtained indicating the intermediacy of *4-(1-bromo-1-methylethyl)-5-phenyl-4,5-dihydro-3H-3,3-pyrazoledicarbonitrile* (6a).[14]

*Syntheses of dimethyl 4-(1-bromo-1-methylethyl)-5-aryl-4,5-dihydro-3*H*-3,3-pyrazoledicarboxylate (*6b–h*).* The syntheses of *6b* and *6e* are described before,[9] and *6c, 6d* and *6f* were prepared analogously (reaction temperature, time and yield given in brackets): *5-(4-Methoxyphenyl), (6c)* (–20 °C, 18 d, 52 %): Dec. at room temperature. Purified by dissolving in chloroform below –10 °C and quickly cooling to –78 °C. ^{1}H NMR (acetone-d_6 –40 °C): δ 7.3–7.1 (4H, AA'XX'-quart.) 5.70 (1H,d, J=10.0 Hz), 4.00 (3H,s), 3.85 (3H,s), 3.82 (3H,s), 3.02 (1H,d, J=10.0 Hz), 1.94 (3H, s), 1.51 (3H,s). *5-(4-Methylphenyl),(6d)* (–20 °C, 14 d, 61 %): Dec. at about 50 °C. Recryst. from dichloromethane–pentane. ^{1}H NMR($CDCl_3$): δ 7.18 (4H,s), 5.75 (1H,d, J=10.0 Hz), 4.01 (3H, s), 3.83 (3H,s), 3.10 (1H,d, J=10.0 Hz), 2.38 (3H,s), 1.94 (3H,s), 1.49 (3H,s). *5-(4-Bromophenyl), (6f)* (–20 °C, 18 d, 71 %): M.p. 98–99 °C (dichloromethane–pentane). Anal. $C_{16}H_{18}Br_2N_2O_4$: C,H. ^{1}H NMR($CDCl_3$): δ 7.5–7.2 (4H, AA'XX'-quart.), 5.75 (1H,d, J=10.0 Hz), 4.00 (3H,s), 3.83 (3H,s), 3.07 (1H,d, J=10.0 Hz), 1.93 (3H,s), 1.50 (3H,s). IR(KBr); 1740 (s), 1540 (m) cm^{-1}.

*Dimethyl 4-(1-chloro-1-methylethyl)-5-phenyl-4,5-dihydro-3*H*-3,3-pyrazoledicarboxylate (*6g*).* Prepared analogously to *6b* from *5c*.[9] Yield 62 %, m.p. 109–110 °C (chloroform–pentane) Anal. $C_{16}H_{19}ClN_2O_4$: C,H,N. ^{1}H NMR($CDCl_3$): δ 7.6–7.3 (5H,m), 5.88 (1H,d, J=10.0 Hz), 4.13 (3H,s), 3.92 (3H,s), 3.44 (1H,d,J=10.0 Hz), 1.90 (3H,s), 1.42 (3H,s). IR (KBr): 1745 (s), 1550 (m) cm^{-1}.

*Dimethyl 4-isopropyl-5-phenyl-4,5-dihydro-3*H*-3,3-pyrazoledicarboxylate (*6h*).* Prepared analogously to *6b* from *5d*.[9] Yield 55 %. ^{1}H NMR($CDCl_3$, –60 °C): δ 7.6–7.1 (5H,m),5.39 (1H,d, J=10.0 Hz), 4.06 (3H,s), 2.76 (1H, 2d, both with J=10.0 Hz), 1.9–1.4 (1H,m), 0.99 (3H,d, J=6.0 Hz), 0.79 (3H,d, J=6.0 Hz).

Decomposition of pyrazolines 6b–h. The decomposition of *6b* and *6e* to give *8b* and *8e*, respectively, is described elsewhere.[9] Following the same procedure *6c, 6d* and *6f* were decomposed. Thus *6c* gave *dimethyl 2-(1-bromo-1-methylethyl)-3-(4-methoxyphenyl)-1,1-cyclopropanedicarboxylate* (8c): Yield 90 %. M.p. 50–52°C (chloroform–pentane). Anal. $C_{17}H_{21}BrO_5$: C,H. ^{1}H NMR($CDCl_3$): δ 7.3–7.1 (4H, AA'XX'-quart.), 3.62 (3H,s), 3.58 (3H,s), 3.43 (3H,s), 3.43 and 3.00 (2H, AB-quart. J=9.0 Hz), 1.97

(3H,s), 1.80 (3H,s). The decomposition products from *6d*, *6f* and *6g* were identified by their ^{1}H NMR spectra to be *dimethyl 2-(1-bromo-1-methylethyl)-3-(4-methylphenyl)-1,1-cyclopropanedicarboxylate* (8d): ^{1}H NMR ($CDCl_3$): δ 7.3–7.1 (4H, AA'XX'-quart.), 3.72 (3H,s), 3.37 (3H,s), 3.44 and 3.04 (2H, AB-quart, J=9.0 Hz), 2.25 (3H,s), 1.92 (3H,s), 1.77 (3H,s): *dimethyl 2-(1-bromo-1-methylethyl)-3-(4-bromophenyl)-1,1-cyclopropanedicarboxylate* (8f): ^{1}H NMR ($CDCl_3$): 7.4–7.1 (4H, AA'XX'-quart), 3.77 (3H,s), 3.45 (3H,s), 3.38 and 2.99 (2H, AB-quart. J=9.0 Hz), 1.95 (3H,s), 1.77 (3H,s); and *dimethyl 2-(1-chloro-1-methylethyl)-3-phenyl-1,1-cycloprropanedi carboxylate* (8g): ^{1}H NMR ($CDCl_3$): δ 7.28 (5H,s), 3.78 (3H,s), 3.43 (3H,s), 3.47 and 2.83 (2H, AB-quart. J=9.0 Hz), 1.78 (3H, s), 1.72 (3H,s), respectively. Similar decomposition of *6h* led to a mixture of cyclopropane *8h* (45 %) and an alkene, *dimethyl 3-methyl-2-phenylbutylidenemalonate* (55 %). Column chromatography gave *8h* in a state pure enough for ^{1}H NMR, while the alkene only was obtained as a mixture with *8h*. *Dimethyl 2-isopropyl-3-phenyl-1,1-cyclopropanedicarboxylate* (*8h*): ^{1}H NMR($CDCl_3$): δ 7.20 (5H,s), 3.77 (3H,s), 3.35 (3H,s), 3.10 (1H,d, J=8.0 Hz), 2.25 (1H, 2d, J=8.0 and 8.8 Hz), 1.8–1.3 (1H,m), 1.10 (3H,d, J=7.0 Hz), 0.95 (3H,d, J=7.0 Hz).

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