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The Reaction between Diazoalkanes and Allylic Halides Carrying Electronegative γ-Substituents. 3. The Crystal Structures of Dimethyl 4-(1-Bromo-1-methylethyl)-5-phenyl-4,5-dihydro-3*H*-pyrazole-3,3-dicarboxylate and Dimethyl 2-(1-Bromo-1-methylethyl)-3-phenyl-1,1-cyclopropane-dicarboxylate

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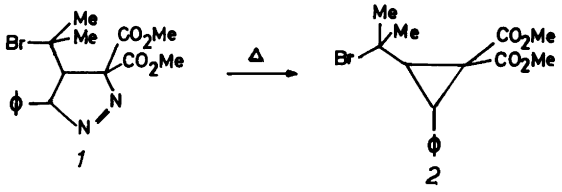
The structures of the title compounds have been determined by X-ray methods. Full-matrix least-squares refinements led to *R*-values of 0.061 (3289) and 0.099 (1989), respectively. (The numbers of observed reflections are in parentheses.)

The compounds are monoclinic with the following unit cell dimensions (at –150 ° C): The pyrazoline compound: a=7.171(2) Å; b=9.790(2) Å; c=25.121(4) Å; β=106.62(2)°; space group $P2_1$, Z=2. The cyclopropane compound: a=10.055(2) Å; b=12.135(2) Å; c=13.278(2) Å; β=103.57(2)°; space group $P2_1/c$, Z=4.

In both compounds the bromoisopropyl group and the phenyl group are situated *trans* with respect to the central ring. Bond lengths and angles are normal. In the cyclopropane compound a rotational disorder in the bromoisopropyl group was observed.

Synthesis of the title compound *1* and its thermal decomposition into *2* is reported earlier (Scheme 1).[1]

The decomposition of 1-pyrazolines to give cyclopropanes could in principle follow two different pathways: One involving a dipolar transition state and one involving diradical intermediates. The former is usually expected when the ring contains charge-stabilizing substituents and the latter pathway is preferred with unsubstituted or alkyl-substituted 1-pyrazolines[2] or when photolytically decomposed.[3] The stereochemical outcome of the decomposition has been at variance. Retention,[4] predominate inversion or lack of stereospecificity[4b] has been observed. In connection with our studies on the decomposition of 1-pyrazolines to give cyclopropanes it was of prime importance to know the



1 *2*

Scheme 1.

0302-4369/83 $2.50

stereochemistry of both the starting material and the product.[5-7]

Stereochemical relations between substituents in 1-pyrazolines are normally determined on the basis of (i) the concertedness of 1,3-dipolar cycloadditions giving retention of the stereochemistry of the starting alkene, along with the stereoselectivity observed when large substituents present in the 1,3-dipole and the dipolarophile interact in the transition state,[8] (ii) ^{1}H NMR coupling constants if vicinal hydrogens are present in the ring,[9] and (iii) the assumption that pseudoaxial hydrogens are located in the deshielding zone of the azo group and thus shifted to higher field relative to pseudoequatorial hydrogens.[9]

During the formation of *1* the bromoisopropyl group in the dipolarophile and the phenyl group in the 1,3-dipole are expected to interact in such a way that a *trans* adduct will be preferred. Furthermore, an observed coupling constant $J_{H_2H_3}$=10.0 Hz is probably due to coupling between two pseudoaxial hydrogens.[9,10] However, since the Karplus equation predicts large coupling constants both for large and small torsion angles, a *cis* relation between the 2- and 3-substituents (torsion angle about 30°) could just as well be justified by the observed coupling constant. The situation is further complicated by the proposed conformational equilibrium for 1-pyrazolines, where pseudoaxial and -equatorial positions are rapidly interchanged.[7-10]

The stereochemistry of the cyclopropane *2* was expected to be easily determined by the vicinal coupling constant, which normally takes its largest value between *cis* protons (torsion angle approx. 0°). Vicinal coupling constants in cyclopropane derivatives are reported to be 8.0–11.2 Hz for *cis* and 5.2–8.0 Hz for *trans* located hydrogens.[11] In dimethyl *trans*-2-methyl-3-phenyl-1,1-cyclopropanedicarboxylate J_{23}=8.2 Hz while in the *cis* analogue J_{23}=10.8 Hz.[12]

The observed coupling constant of 9.0 Hz for *2* indicates a *cis* relation between the phenyl group and the bromoisopropyl group, implying an inversion of the stereochemistry during the thermolytic decomposition which in turn indicates the intermediacy of a diradical.[3] On the other hand, compound *1* carries highly polar substituents and the rate of decomposition increases with enhanced charge-stabilizing capacities of the substituents.[6] Faced with the above-mentioned ambiguities with regard to the precise stereochemistry of *1* and *2*, a study of these compounds by X-ray diffraction was initiated.

EXPERIMENTAL

Data for the measurements of cell dimensions and intensity data were collected on a SYNTEX $P\bar{1}$ diffractometer with –150 ° C at the crystal site using graphite crystal monochromated Mo$K\alpha$ radiation (λ=0.71069 Å). Cell parameters were determined by a least-squares fit to the diffractometer settings for 15 general reflections. Intensity data were collected with the $\theta/2\theta$ scan technique, scan speed 3–6° min^{-1} (2θ) depending on the intensity; scan width 1.6° (2θ). All intensities in a quadrant of reciprocal space within sin θ/λ=0.63 Å^{-1} for *1* and sin θ=0.54 Å^{-1} for *2* were measured. Background counts were taken at each of the scan limits for 0.35 times the scan time. Three standard reflections were measured after every 100 reflections and the intensities of the data sets were adjusted according to the drift in the standard reflections. The numbers of reflections recorded for the two compounds were 3841 for *1* and 2332 for *2*. Of these 3289 (*1*) and 1989 (*2*) with $I>2.5\sigma(I)$ were retained for the structure determinations. The estimate of the standard deviation of the intensity was based on counting statistics with an additional term of 5 % of the net intensity. The data were corrected for Lorentz and polarization effects, but not for absorption or extinction.

A description of the computer programs applied for the structure analyses is given in Ref. 13. The quantity minimized in the full-matrix least-squares program was $\Sigma w\Delta F^2$, where w is the inverse of the variance of the observed structure factor.

Atomic form factors were those of Doyle and Turner[14] for Br, O, N and C, and of Stewart, Davidson and Simpson[15] for H.

CRYSTAL DATA

1. Dimethyl 4-(1-bromo-1-methylethyl)-5-phenyl-4,5-dihydro-3*H*-pyrazole-3,3-dicarboxylate, $C_{16}H_{19}BrN_2O_4$, m.p. 104–105 °C (ether–pentane). Monoclinic, a=7.171(2) Å; b=9.790(2) Å; c=25.121(4) Å; β=106.62(2)°; V=1689.9 Å^3, (t= –150 °C). M=383.25; Z=2; $F(000)$=784; μ(Mo$K\alpha$)=26.0 cm^{-1}; D_x=1.506 g cm^{-3}. Space group $P2_1$ (No. 4).

2. Dimethyl 2-(1-bromo-1-methylethyl)-3-phenyl-1,1-cyclopropanedicarboxylate,

Table 1. Fractional atomic parameters and standard deviations.

Atom	*x*	*y*	*z* (Cpd. *1*)	*x*	*y*	*z* (Cpd. *2*)
BR	0.8838(1)	0.8755(0)	0.6234(3)	0.0771(1)	0.0466(0	0.1285(0)
C10	0.6207(12)	0.9493(19)	0.5813(13)	0.2051(18)	0.0851(16)	0.2589(6)
C11	0.5745(12)	0.8885(11)	0.5227(3)	0.3334(8)	0.1347(6)	0.2338(6)
C12	0.6426(13)	1.1047(10)	0.5783(4)	0.2394(3)	–0.0423(2)	0.3259(2)
C1	0.4087(11)	0.7626(3)	0.6171(0)	0.1751(8)	0.2042(6)	0.4226(6)
C2	0.4673(10)	0.9138(8)	0.6112(3)	0.1294(8)	0.1668(6)	0.3087(6)
C3	0.5099(11)	0.9676(8)	0.6710(3)	0.0403(8)	0.1386(6)	0.3828(6)
C4	0.4443(11)	1.1129(9)	0.6781(3)	–0.0977(8)	0.1894(6)	0.3754(6)
C5	0.2574(12)	1.1564(9)	0.6501(4)	–0.1451(8)	0.1984(6)	0.4634(6)
C6	0.1999(12)	1.2894(10)	0.6583(4)	–0.2766(9)	0.2440(7)	0.4580(7)
C7	0.3263(13)	1.3776(10)	0.6949(4)	–0.3548(9)	0.2795(7)	0.3655(7)
C8	0.5134(12)	1.3332(10)	0.7235(4)	–0.3061(9)	0.2690(7)	0.2768(7)
C9	0.5715(12)	1.1997(9)	0.7157(3)	–0.1761(8)	0.2255(6)	0.2817(6)
C13	0.5681(11)	1.6554(8)	0.6245(3)	0.2944(9)	0.1520(6)	0.5007(6)
C14	0.8429(13)	0.5515(10)	0.6868(4)	0.3663(9)	0.0259(7)	0.6341(7)
C15	0.2337(11)	1.7180(9)	0.5704(3)	0.1536(8)	0.3249(6)	0.4427(6)
C16	–0.0036(13)	0.5477(10)	0.5399(4)	0.1883(10)	0.4637(6)	0.5734(7)
O1	0.6747(8)	1.6436(6)	0.6774(2)	0.2548(5)	0.0813(4)	0.5626(4)
O2	0.1651(8)	0.5994(7)	.5817(2)	0.2070(5)	0.3491(4)	0.5415(4)
O3	0.5923(9)	0.5898(6)	0.5864(6)	0.4111(6)	0.1741(4)	0.5000(4)
O4	0.1676(8)	0.7819(7)	0.5275(2)	0.0930(6)	0.3887(4)	0.3781(4)
N1	0.4013(9)	0.8724(8)	0.6978(3)			
N2	0.3461(9)	0.7651(7)	0.6702(3)			
H111	0.431	0.926	0.498	0.382	0.077	.202
H112	0.572	0.777	0.525	0.398	0.162	.300
H113	0.686	0.922	0.503	0.308	0.198	.185
H121	0.754	1.127	0.557			
H2	0.354	0.964	0.581	0.111	0.205	.241
H122	0.691	1.147	0.621			
H123	0.504	1.149	0.555			
H3	0.665	0.971	0.698	0.005	0.069	.407
H5	0.158	1.087	0.622	–0.142	0.222	.220
H6	0.055	1.324	0.636	–0.311	0.249	.517
H7	0.283	1.482	0.701	–0.443	0.309	.365
H8	0.611	1.398	0.753	–0.361	0.296	.212
H9	0.717	1.164	0.738	–0.142	0.222	.220
H141	0.921	0.550	0.732	0.330	–0.026	.678
H142	0.942	0.591	0.664	0.429	0.080	.678
H143	0.795	0.449	0.673	0.421	–0.017	.592
H161	–0.052	0.450	0.553	0.233	0.471	.649
H162	0.033	0.534	0.500	0.089	0.479	.561
H163	–0.124	0.623	0.533	0.233	0.513	.532

$C_{16}H_{19}BrO_4$, m.p. 61–62 °C (heptane). Monoclinic, a=10.055(2) Å; b=12.135(2) Å; c=13.278(2) Å; β=103.57(2)°; V=1574.9 Å^3, (t= –150 °C). M=355.23; Z=4; F(000)=728; μ(Mo$K\alpha$)=27.8 cm^{-1}; D_x=1.498 g cm^{-3}. Space group $P2_1/c$ (No. 14).

STRUCTURE DETERMINATIONS

The structures were determined by Patterson methods followed by successive Fourier syntheses. Positions were calculated for hydrogen atoms and these were included as fixed contributors in the least-squares calculations. During the

Table 2. Structural data.

Bond	Bond lengths (A) Cpd. *1*	Cpd. *2*
BR–C10	2.015(8)	
C10–C11	1.534(11)	1.530(12)
C10–C12	1.533(13)	
C2–C10	1.539(11)	1.496(12)
C1–C2	1.566(11)	1.542(11)
C1–C3		1.544(11)
C2–C3	1.538(10)	1.516(12)
C1–N2	1.524(9)	
N1–N2	1.259(10)	
C3–N1	1.493(10)	
C3–C4	1.524(11)	1.501(12)
C–C(Ph)*	1.396(11)	1.385(10)
C1–C13	1.524(10)	1.527(11)
C1–C15	1.516(11)	1.513(12)
C13–O1	1.336(9)	1.313(10)
C13–O3	1.206(9)	1.206(11)
O1–C14	1.471(10)	1.455(11)
C15–O2	1.324(10)	1.328(10)
C15–O4	1.219(9)	1.209(10)
O2–C16	1.449(10)	1.476(10)

Torsion angles (°)	Cpd. *1*	Cpd. *2*
C10–C2–C3–C4	85.7(8)	–135.5(8)
C10–C2–C1–C13	34.5(10)	–7.2(12)
H2–C2–C3–H3	145	135
C10–C2–C1–C15	–92.8(8)	141.7(8)

Angles between planes	Cpd. *1*
C1–N2–N1–C3 and C1–C2–C3	22.9(10)
C1–N2–N1–C3 and C4–C3–C1–C15	91.4(8)
C1–N2–N1–C3 and phenyl	85.5(8)

Bond angles (°)	Cpd. *1*	Cpd. *2*
BR–C10–C11	106.5(6)	
BR–C10–C12	106.8(6)	
BR–C10–C2	110.8(5)	
C2–C10–C11	113.1(7)	112.2(7)
C2–C10–C12	110.3(7)	
C1–C2–C10	120.7(6)	124.3(7)
C1–C2–C3	102.6(6)	61.1(5)
C3–C2–C10	115.4(6)	125.2(7)
C1–C3–C4		122.1(7)
C2–C3–C4	116.9(7)	122.9(7)
C2–C3–N1	104.1(6))	
C4–C3–N1	108.1(6)	
C3–N1–N2	113.2(6)	
N1–N2–C1	118.1(6)	
N2–C1–C13	107.6(6)	
N2–C1–C15	107.2(6)	
C2–C1–C13	116.9(6)	123.3(7)
C2–C1–C15	112.8(6)	115.9(7)
C3–C1–C13		120.1(7)
C3–C1–C15		114.0(7)
C–C–C(Ph)	119.9(5)	120.0(4)
C3–C4–C5	120.7(7)	118.7(8)
C3–C4–C9	118.9(7)	120.9(8)
C1–C13–O3	122.9(7)	120.9(8)
C1–C13–O1		113.0(7)
C13–O1–C14	115.0(6)	114.2(7)
C1–C15–O4	124.2(8)	124.3(7)
C1–C15–O2		110.3(7)
C15–O2–C16	115.7(7)	116.2(7)
O3–C13–O1	125.0(7)	126.0(8)
O4–C15–O2	124.5(7)	125.4(8)
C11–C10–C12	109.5(7)	112.1(6)
C2–C1–C3		58.7(5)
C13–C1–C15	108.8(7)	113.8(7)
C2–C1–N2	102.9(6)	

refinements a disorder in the structure of *2* was revealed. The bromine atom of the bromoisopropyl group turned out to be partially interchanged with one of the methyl groups (C12) corresponding to a rotation of 120° about the C2–C10 bond. The positions of the two pairs of atoms could not be resolved; the model was thus refined with pseudo atoms situated at the Br and C12 sites where the population factors also were parameters. The results showed that about 1/4 of the bromine is replaced by methyl and *vice versa* at C12. Obviously no determination of the C10–C12 and C10–Br bond lengths could be made; the disorder probably also is the reason for the rather poor agreement factors arrived at for this compound.

The refinements converged to conventional R factors of 0.061 for *1* and 0.099 for *2*. The R_w were 0.068 and 0.14; the $S=[\Sigma w\Delta F^2/(m-n)]^{1/2}$ were 2.0 and 5.0, respectively.

Final atomic coordinates are listed in Table 1. Tables of the thermal parameters and the structure factor listings are available from the authors.

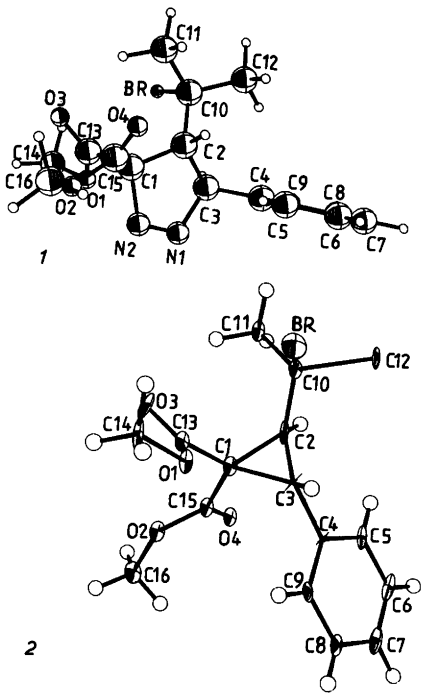


Fig. 1. ORTEP drawings of compounds *1* and *2*.

DISCUSSION

ORTEP drawings of the molecules are shown in Fig. 1 where the numbering scheme of the atoms is also indicated. In Table 2 the structural data are listed. Estimated standard deviations are calculated from the variance–covariance matrices.

As demonstrated earlier,[16] the 1-pyrazoline ring possesses envelope conformation with C3, N1, N2 and C1 situated in a plane forming an angle of 22.9° with the plane through C1, C2 and C3. The ring plane of the phenyl group forms an angle of 85.5° with the plane through C3, N1, N2 and C1. As may be seen from Fig. 1, the phenyl group and the bromoisopropyl group are situated *trans* to each other in both compounds.

For *1* the large groups positioned at C2 and C3 are placed pseudoequatorially with the torsion angle C10–C2–C3–C4 being 85.7°. The torsion angles C10–C2–C1–C13 and C10–C2–C1–C15 are 34.5 and 92.8°, respectively. The distance between the bromine atom and C3 is short (3.35 Å) compared to the sum of the van der Waals' radii (3.45 Å). If this is also the case in solution, the electrons of the bromine atom may contribute significantly to the stabilizing of a developing positive charge on C3 during thermolysis, and may explain the differences in thermolysis rates between brominated and non-brominated analogues of *1*.[5,17]

For the cyclopropane derivative *2* the torsion angle C10–C2–C3–C4 is 135.5°. Thus, the observed coupling constant in NMR between the adjacent hydrogens is larger than expected from the Karplus equation and from analogues found in the literature.[9,18]

Bond lengths and bond angles have the expected values in both compounds. The packing arrangements in the crystals are also quite normal with intermolecular separations to be expected from the van der Waals' radius sums.

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