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The Reaction between Diazoalkanes and Allylic Halides Carrying Electronegative γ-Substituents. 4. Conformational Equilibria of Highly Substituted 1-Pyrazolines

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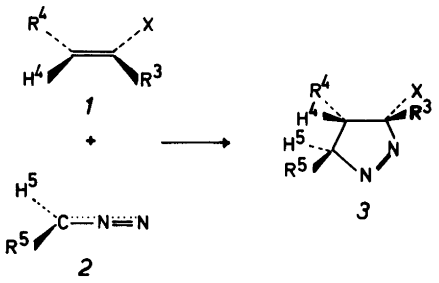
Some di- and trisubstituted 1-pyrazoline-3-carbonitriles were synthesized and the coupling constants between vicinal protons were measured. In those cases where only one large substituent is present, the pseudoequatorial position is preferred. When two large groups are present *trans* to each other in vicinal position, the dipseudoaxial conformation is preferred. The compounds with preference for the dipseudoaxial conformation unexpectedly gave only cyclopropane derivatives when decomposed.

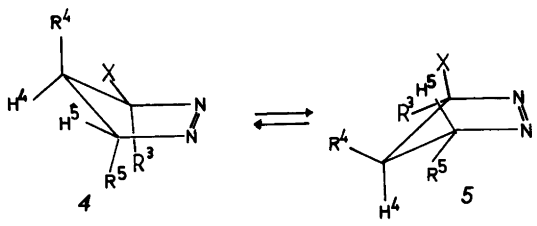
In our studies of the thermal decomposition of 1-pyrazolines substituted with cyano- or ester groups in the 3-position, 1,3-dipolar cycloaddition reactions of diazoalkanes and α,β-unsaturated diesters and dinitriles led to formation of 1-pyrazolines with the same stereochemical relation between the 4- and 5-substituents.[1–3] On the basis of the coupling constants between the vicinal hydrogens, and the sterical restrictions of 1,3-dipolar cyloaddition,[4] the substituents were assumed to be *trans* to each other (Scheme 1).

The *trans* structure of *3d* was verified by X-ray diffraction methods.[5] In the cases where $R^3 \neq X$, the stereochemistry of the starting alkene was assumed to be preserved in the 1-pyrazoline, based on the concertedness of the 1,3-dipolar cycloaddition reactions.[4]

As pointed out earlier,[6–7] the 1-pyrazoline ring system equilibrates in solution between the two conformations with C_s symmetry, where pseudoaxial and -equatorial positions are rapidly interchanging (Scheme 2). In analogy with cyclohexane systems, the relative population of each conformation is controlled by sterical interactions between substituents, and it is generally accepted that the conformer with the highest number in pseudoequatorial positions will be the most



Scheme 1. *1a*, $X=R^3=CN$, $R^4=CBrMe_2$; *1b*, $X=R^3=CN$, $R^4=Bu^t$; *1c*, X=CN, $R^3=Me$, $R^4=CBrMe_2$; *1d*, X=CN, $R^3=Bu^t$, $R^4=CBrMe_2$; *1e*, $X=R^3=CO_2Me$, $R^4=CBrMe_2$; *2a*, $R^5=H$; *2b*, $R^5=Me$; *2c*, $R^5=Ph$; *2d*, $R^5=Bu^t$; *3*, see Table 1.



Scheme 2.

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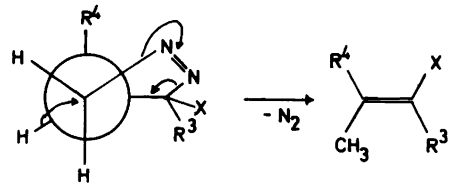
stable.[6] The observed vicinal coupling constants must, as a consequence of the dynamic situation, appear as the weighted average of the coupling constant for each conformer. Based on model substances, coupling constants of 1-pyrazolines have been used to calculate the conformational distribution in solution.[8]

The role of conformational equilibrium of 1-pyrazolines in determining the proportion between alkene and cyclopropane derivatives formed during decomposition is discussed in the literature.[6-7] A general view is that alkenes are formed *via* migration of a pseudoequatorial group (hydrogen or alkyl) from C 4 to replace the leaving nitrogen at C5 (Scheme 3).



Scheme 3.

Consequently, knowledge of the conformational situation for 1-pyrazoline derivatives is essential for prediction of the decomposition products, and for consideration of the mechanism of the pyrolysis reaction.

^{1}H NMR data of 1-pyrazolines prepared according to Scheme 1 are given in Table 1.

The stereochemistry of the alkenes *1c* and *1d* (Scheme 1) deserves some comment. *1d* was synthesized by the Wittig reaction between triphenylphosphonium isobutylide and 3,3-dimethyl-2-oxobutyronitrile followed by allylic bromination with *N*-bromosuccinimide (NBS). ^{1}H NMR of the reaction mixture from the Wittig reaction showed that a stereochemically pure alkene was formed (doublet at 5.8 ppm with splitting of 9.5 Hz). From the nature of the Wittig reaction it is likely that formation of the least sterically hindered alkene is preferred[11] and for that reason the product was assumed to have the

Table 1. Chemical shifts and vicinal coupling constants of ring protons in pyrazolines *3*.

Compound	X	R^3	R^4	R^5	δ_{H^4}	δ_{R^5}	δ_{H^5}	$J_{H_4H_5}$/Hz *cis*	$J_{H_4H_5}$/Hz *trans*	Solvent[a]	Temp. °C	Ref.
3a	CN	CN	Bu^t	H	2.53	5.41	4.47	7.8	11.5	1	–130	*b*
3a	CN	CN	Bu^t	H	2.51	5.18	4.67	8.3	10.7	1	–50	*b, 9*
3b	Me	MeCO	Me	Ph	1.92	–	4.68	–	10.4	2	30	6a
3c	CO_2Me	CO_2Me	Bu^t	H	–	4.83	4.30	8.4	10.0	2	30	8
3d	CO_2Me	CO_2Me	$CBrMe_2$	Ph	3.12	–	5.77	–	10.0	2	30	2, 3
3e	MeCO	Me	Me	Ph	1.60	–	4.90	–	9.8	2	30	6a
3f	CN	CN	$CBrMe_2$	H	3.62	5.71	5.37	8.0	8.0	3	–70	1
3g	CN	CN	$CBrMe_2$	Ph	–	–	6.23		8.7	4	–52	2
3h	CN	CN	$CHMe_2$	H	2.36	5.25	4.43	7.3	8.7	2	–60	10
3i	CO_2Me	CO_2Me	Ph	Me	3.60	–	4.95	–	8.5	2	30	6a
3j	CO_2Me	CO_2Me	$CBrMe_2$	Me	3.20	–	5.62	–	7.8	2	30	*b*
3k	CO_2Me	CO_2Me	Bu	H	–	4.89	4.21	8.3	7.8	2	30	8
3l	CO_2Me	CO_2Me	Et	H	–	4.86	4.24	8.3	7.4	2	30	8
3m	CN	CN	$CBrMe_2$	Me	3.16	–	5.43	–	6.7	3	–60	*b*
3n	CO_2Me	CO_2Me	Me	H	2.82	4.82	4.27	8.0	6.2	2	30	8
3o	CN	Me	$CBrMe_2$	Me	3.00	–	5.11	–	5.4	2	30	*b*
3p	CN	Bu^t	$CBrMe_2$	Me	–	–	5.21	–	4.9	2	30	*b*
3q	CN	Bu^t	$CBrMe_2$	H	2.70	5.28	4.76	9.3	4.1	2	30	*b*
3r	CN	CN	Bu^t	Bu^t	2.74	–	5.48	–	3.2	3	–30	*b*
3r	CN	CN	Bu^t	Bu^t	2.83	–	5.54	–	3.1	3	–60	*b*
3r	CN	CN	Bu^t	Bu^t	2.91	–	5.62	–	2.1	3	–90	*b*
3s	CN	CN	$CBrMe_2$	Bu^t	3.22	–	5.57	–	2.8	4	–60	*b*

[a] Solvents: 1. $CHCl_2F$, 2. $CDCl_3$, 3. acetone-d_6, 4. CCl_3F. [b] This paper.

Z-configuration. The resonance line for the vinylic proton of *1d* was positioned at 6.30 ppm, which corresponds to introduction of a bromine atom in the allylic position with retention of the alkene stereochemistry.[12] The nonbrominated analogue of *1c* was formed as a 1:1 mixture of *Z*- and *E*-isomers, which were separated by fractional distillation. The shifts of the vinylic protons were 5.83 and 6.05 ppm, respectively. Bromination of both isomers resulted in the same allyl bromide with its vinylic resonance line at 6.33 ppm, very close to that of *1d*.

As mentioned above, observed vicinal coupling constants appear as weighted averages according to the conformational equilibria positions (Scheme 2). The torsion angles between *cis* substituents are 20–30° in both conformers,[5,8] and according to the Karplus equation,[13] the *cis* coupling constant will be large independent of the conformational distribution. In contrast, torsion angles between *trans* hydrogens will change from about 85° when situated in diequatorial positions (conformer *4*), to about 145° when situated in diaxial positions (conformer *5*).[5] As a consequence of the Karplus equation, the coupling constant between the *trans* hydrogens will be small when *4* is dominating, and large whenever conformer *5* is the most stable one.[8] In Table 1 the compounds appear in order of decreasing *trans* coupling constants.

At this point one must consider that differences in the substitution pattern may affect the size of the coupling constants in a somewhat unpredictable way.[13] However, these effects are small compared to the differences from the top to the bottom of Table 1 and a change above 1.5 Hz is likely to indicate a change in the conformational equilibrium.

The 4-alkylsubstituted diesters *3n, 3l, 3k* and *3c* show a steady increase in the *trans* coupling constant with increasing size of R^4 (Me<Et<Bu<*t*-Bu).[8] Hence, it is obvious that when other substituents are small, a large R^4 will prefer the pseudoequatorial position (conformer *5*). This effect may be due to the repulsive interaction between the hydrogens of R^4 in axial position and the π-electrons of the azo group. The preference for conformer *5* is also seen for the compounds *3a, 3d, 3f* and *3g*, where only one large substituent is present in the ring (the bromoisopropyl group is regarded as similar in size to a tertiary butyl group). In this connection it should be mentioned that while *3c* is reported to be "locked" in conformation *5* below –15 °C,[8] conformer *4* of the corresponding dinitrile (*3a*) is still significant at –50 °C, as seen by a further increase of J_{trans} when decreasing the temperature to –130 °C.

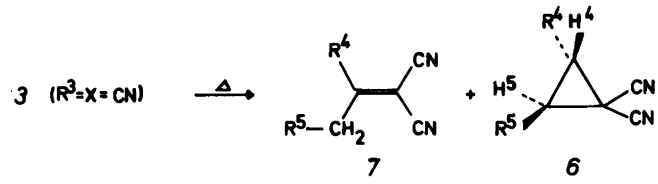
However, the situation changes completely when more than one large group are present. In going from *3f* to *3m* to *3s* the 3- and 4-substituents are kept constant, while the 5-substituent increases from hydrogen through methyl to *tert*-butyl. The result is a drastic reduction of the coupling constant (8.0–6.7–2.8 Hz), which implies a complete change in the conformational equilibrium. In *3s* the bromoisopropyl group and the *tert*-butyl group have a strict preference for the pseudoaxial position, which is in sharp contrast to earlier observations.[6–8] The same situation is seen for compounds *3q* and *3r, i.e.* whenever two large vicinal groups are present in *trans* positions. The slightly higher coupling constant of *3p* relative to *3q* may indicate that the interaction between two pseudoaxial substituents at C3 and C5 (Me, Bu^t) becomes significant, thus reducing the stability of conformer *4*.

In this connection it is interesting to note the temperature dependency in the ^1H NMR spectra of *3r*. When the temperature is reduced from –30 °C to –60 °C and further to –90 °C, the coupling constant drops from 3.2 to 3.1 to 2.1 Hz. Since a reduction in temperature will favor the most stable conformer, this drop in coupling constants represent additional evidence for the two *tert*-butyl groups being in pseudoaxial positions (conformer *4*).

Another interesting feature of the spectra of *3r* is the increased splitting of the lines from the *tert*-butyl groups, indicating hindered rotation about one of the C–CMe_3 bonds at low temperature (see Experimental). Model considerations indicate that this is due to an interaction between the *tert*-butyl group at C5 and the pseudoaxial cyano group at C3.

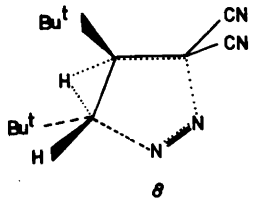
The thermal decomposition into mixtures of cyclopropanes and alkenes of the 1-pyrazoline-3,3-dinitriles appearing in Table 1 is summarized in Table 2 (Scheme 4).

We have earlier suggested that the preference for alkene formation in nonpolar solvents is due to the lack of external stabilization of the developing charge at C5, and that sterical effects are important in this connection. Since we have



Scheme 4.

found that pyrazolines *3r* and *3s* exist entirely in conformation *4* with H^4 in the correct position to replace the leaving nitrogen at C5, one should expect high yields of alkenes from these compounds. However, when decomposed both in polar and nonpolar solvents, *3r* and *3s* gave cyclopropanes as the only products. An explanation for this inconsistency with earlier assumptions may be found in the serious compression of the torsion angle between the large substituents at C4 and C5 in the transition state leading to the alkene. The hypothetically formed alkene will have a neopentyl and a *tert*-butyl group on the same vinylic carbon atom, and if the transition state has some product-like character, serious steric hindrance is to be expected (*8*).



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 A60A or Varian HA 100 15D spectrometer operating at 98 MHz, ^{13}C NMR spectra on a JEOL FX-60 FT NMR spectrometer and mass spectra on an AEI MS 902 instrument. Elemental analyses were performed by I. Beetz, West Germany.

Diazoalkanes. Diazomethane,[14] diazoethane,[15] phenyldiazomethane[16] and 1-diazo-2,2-dimethylpropane[17] were prepared according to procedures described in the literature. Instead of the usual ethereal solutions, diazoalkanes in $CDCl_3$, CHF_3, $CHCl_2F$ and CCl_2F_2 were prepared in order to study their addition to alkenes in ^{1}H NMR tubes.

Alkenes. Alkylidenemalonate *1e*[18] and alkylidenemalononitrile *1a*[19] were prepared according to literature procedures. *1b* was synthesized by the Knoevenagel condensation between 2,2-dimethylpropanal and malononitrile with Amberlite IR-45 as catalyst.[20]

2,4-Dimethyl-2-pentenoic nitrile (E+Z). Diethyl 1-cyano-ethanephosphonate was prepared in 0.1 mol scale,[21] and this "one-pot olefin synthe-

Table 2. Decomposition of 1-pyrazoline-3,3-dinitriles *3* (R^3=X=CN) to give cyclopropanes *6* and alkenes *7*.[a]

Compound	Solvent: ether		Solvent: methanol		Ref.
	6	*7*	*6*	*7*	
3a	27	73	84	16	[b]
3f	9	91	100	0	1
3g	100	0	100	0	2
3h	–	–	17	83	10
3r	100	0	–	–	[b]
3s	100	0	100	0	[b]

[a] Yield in per cent. [b] This paper.

sis" was completed by addition of 0.1 mol 2-methylpropanal in THF at –40 °C. After 1 h at ambient temperature, the reaction mixture was quenched with aq. ammonium chloride (150 ml, 20 %) and extracted with ether (400 ml). After drying and evaporation, ^{1}H NMR of the residue indicated approx. 1:1 mixtures of the isomeric alkenes. Separated by fractional distillation. *Isomer A:* 2.9 g, b.p.$_{14}$: 39–41 °C. ^{1}H NMR (CCl_4): δ 1.04 (6H,d, J=7.0 Hz), 1.8–1.9 (3H,m), 2.5–2.9 (1H,m), 5.83 (1H, 2m, J=10.0 Hz). *Isomer B:* 3.7 g, b.p.$_{14}$: 48–50 °C. ^{1}H NMR (CCl_4): δ 1.03 (6H,d,J=7.0 Hz), 1.85 (1H,d,J=1.0 Hz), 2.4–2.8 (1H,m), 6.05 (1H,2d, J_1=10.0 Hz, J_2=1.0 Hz). *A+B:* Overall yield: 6.6 g (61 %). Anal. $C_7H_{11}N$: C,H. IR (film): 2240 and 1650 cm^{-1}.

4-Bromo-2,4-dimethyl-2-(Z)-pentenoic nitrile (1c). 2,4-Dimethyl-2-pentenoic nitrile (1:1, *E+Z*) (3.7 g, 0.03 mol), was dissolved in tetrachloromethane (75 ml), added NBS (6.04 g, 0.03 mol) and dibenzoyl peroxide (50 mg) and refluxed for 1 h. After cooling, succinimide was filtered off and the product distilled. B.p.$_{0.3}$: 56–59 °C. 4.2 g (66 %). Anal. $C_7H_{10}BrN$: C,H. ^{1}H NMR (CCl_4): δ 1.97 (3H,d J=1.0 Hz), 2.07 (6H,s), 6.33 (1H, q, J=1.0 Hz). IR (film): 2250, 1650 cm^{-1}. MS: m/e 188+186 (M^+, 30 %), 107 (M^+–Br, 100 %).

*2-*tert*-Butyl-4-methyl-2-(Z)-pentenoic nitrile.* 2-Methyl-propyltriphenylphosphonium bromide (28.5 g, 0.07 mol) was slurried in benzene (360 ml) under nonaqueous conditions and inert atmosphere. A 15 % solution of butyllithium in hexane (46 ml, 0.07 mol) was added at 0 °C. To the reddish solution of the phosphonium ylide 3,3-dimethyl-2-oxo-butyronitrile[22] (8.0 g, 0.07 mol) in benzene (70 ml) was added over a period of 30 min. The mixture was stirred 1 h at ambient temperature, refluxed for 5 h and worked up in the usual manner. Traces of triphenylphosphine oxide were removed by dissolving in pentane and eluting through a short column of alumina. After fractional distillation 2.6 g (24 %) of acceptable purity (GLC>85 %) was obtained. B.p.$_{12}$: 65–68 °C. ^{1}H NMR (CCl_4): δ 1.05 (6H,d, J=10.0 Hz), 1.13 (9H,s), 2.6–3.0 (1H,m), 5.81 (1H,d, J=10.0 Hz).

*4-Bromo-2-*tert*-butyl-4-methyl-2-(Z)-pentenoic nitrile* (1d). The nonbrominated alkene from above (2.1 g, 0.014 mol) was dissolved in tetrachloromethane (25 ml), NBS (2.47 g, 0.014 mol) and dibenzoyl peroxide (25 mg) was added. After 1 h reflux, ^{1}H NMR showed complete bromination. Yield 1.9 g (59 %), b.p.$_{0.5}$: 56–58 °C. Anal. $C_{10}H_{16}BrN$: C,H. ^{1}H NMR ($CDCl_3$): δ 1.20 (9H,s), 2.07 (6H,s), 6.30 (1H,s). IR (film): 2245, 1650 cm^{-1}. MS: *m/e* 231–229 (M^+, 14 %) 150 (M^+–Br, 100 %).

*c-4-(1-Bromo-1-methylethyl)-3,t-5-dimethyl-4,5-dihydro-3*H*-pyrazole-3-carbonitrile* (3o). An ether solution of *1c* (1.0 g, 5.3 mmol) and diazoethane (1 g, 18 mmol) was left in the dark at 5 °C for 9 d. After evaporation the product was recrystallized from ether–pentane. 1.1 g (85 %), m.p. 82–85 °C (dec). Anal. $C_9H_{14}BrN$: C,H. ^{1}H NMR ($CDCl_3$): δ 1.59 (3H,d, J=7.3 Hz), 1.80 (3H,s), 1.90 (3H,s), 1.95 (3H,s), 3.0 (1H,m), 5.11 (1H,2q, J=7.3 Hz, sep. of quartets: 5.4 Hz) ^{13}C NMR ($CDCl_3$): δ 20.5–29.3–31.2–33.3 (4×Me), 62.2 (C4), 63.0 (*C*BrMe$_2$) 85.1 (C3), 91.0 (C5), 117.3 (C≡N). IR (KBr): 2250, 1555 cm^{-1}.

*c-4-(1-Bromo-1-methylethyl)-3-*tert*-butyl-4,5-dihydro-3*H*-pyrazole-3-carbonitrile* (3q). An ether solution of *1d* (0.5 g, 2.2 mmol) and diazomethane (0.42 g, 10 mmol) was left in the dark at room temperature for 15 d. ^{1}H NMR of the reaction mixture showed complete reaction. Yield 0.54 g (91 %). M.p. 81–83 °C (dec.-chloroform–pentane). Anal. $C_{11}H_{18}BrN$: C,H,N. ^{1}H NMR ($CDCl_3$): δ 1.1 (9H,s), 1.78 (3H,s), 1.98 (3H,s), ABX-system: υ_X=2.70, υ_B=4.76, υ_A=5.28, J_{AB}=19.4 Hz, J_{AX}=4.1 Hz, J_{BX}=9.3 Hz. IR (KBr): 2250, 1555 cm^{-1}.

The reaction between 2b *and* 1a. To a solution of *2b* in CCl_3F cooled to –60 °C was added *1a* dissolved in acetone-d_6 until the yellow color of diazoalkane disappeared (approx. 1 mol eqv. required). The ^{1}H NMR spectrum of the solution was recorded immediately at –60 °C and showed the formation of *3m*: δ 1.74 (3H,d,J=6.7 Hz). 2.00 (3H,s),2.16 (3H,s), 3.16 (1H,d, J=6.7 Hz). 5.43 (1H,2q, J=6.7 Hz, sep. of quartets. 6.7 Hz). When heated, nitrogen was evolved, leaving unidentified material behind.

The reaction between 2a *and* 1b. *1b* (0.5 g, 3.7 mmol) was dissolved in min. amounts of ether, cooled to –78 °C, and a 2 M ethereal solution of *2a* (1.9 ml, 3.8 mmol) was added. After 1 h pentane was added and the precipitated white solid was quickly filtered off and stored at –78 °C. The crystals were dissolved in cold $CHCl_2F$, and ^{1}H NMR spectra run at –50 °C and –130 °C, thus identifying the structure *3a*; *–50 °C*: δ 1.20 (9H,s), ABX-system: υ_X=2.51, υ_A=5.18, υ_B=4.67, J_{AB}=18.2 Hz, J_{AX}=8.3 Hz, J_{BX}=10.7 Hz. *–130 °C*: δ 1.21 (9H,s), ABX-system: υ_X=2.53, υ_A=5.41, υ_B=4.47, J_{AB}=18.0 Hz, J_{AX}=7.8 Hz, J_{BX}=11.5 Hz.

Decomposition of 3a. 100 mg *3a* was dissolved in methanol at room temperature under vigorous evolution of nitrogen. The product was shown by ^{1}H NMR to consist of an 84:16 mixture of 2-*tert*-butyl-1,1-cyclopropanedicarbonitrile[23] and 1,2,2-trimethylpropylidenemalononitrile.[24] In

ethereal solution the evolution of nitrogen was slower, giving the same products in 27:73 ratio.

The reaction between 2d *and* 1a. To a solution of *1a* (1.0 g, 5.0 mmol) in ether (5 ml) *2d* (0.5 g, 5.1 mmol) in ether (2.5 ml) was added at –78 °C. The immediate disappearance of the yellow color of diazoalkane without any gas evolution indicated the formation of a pyrazoline, which after some time precipitated from the solution. After filtration, the crystals were quickly dissolved in cold CCl_3F and ^1H NMR spectrum run at –60 °C identified the crystals as *3s:* δ 1.10 (9H,s), 1.90 (3H,s), 2.15 (3H,s), 3.22 (1H,d, J=2.8 Hz), 5.57 (1H,d, J=2.8 Hz).

Decomposition of 3s. *3s* decomposed readily at room temperature, either neat, in methanol or in ether to give a single product which was identified as trans-*2-(1-bromo-1-methylethyl)-3-tert-butyl-1,1-cyclopropanedicarbonitrile.* M.p. 110–111 °C (ether–pentane). Anal. $C_{12}H_{17}BrN_2$: C,H,N. ^{H} NMR ($CDCl_3$): δ 1.32 (9H,s), 1.88 (3H,s), 1.97 (3H,s), 2.07 (1H,d, J=10.0 Hz), 2.47 (1H,d,J=10.0 Hz). MS: m/e 189 (M^+–Br, 2 %), 57 ($C_4H_9^+$, 100 %).

The reaction between 2d *and* 1b. To a solution of *1b* in acetone-d_6 at –78 °C was added an approx. equimolar amount of *2d* in CCl_3F under immediate disappearance of the color of the diazoalkane. ^1H NMR spectra were run at –30 °C, –60 °C and –90 °C, showing the formation of *3r:*

–30 °C: δ 1.06 (18H, broad s), 2.74 (1H,d, J=3.2 Hz), 5.48 (1H,d, J=3.2 Hz).

–60 °C: δ 1.02 (3H,s), 1.07 (12H, broad s), 1.17 (3H,s) 2.83 (1H,d, J=3.1 Hz), 5.54 (1H,d, J=3.1 Hz).

–90 °C: δ 0.86 (3H,s), 1.09 (9H, broad s), 1.17 (3H,s) 1.37 (3H,s), 2.91 (1H,d, J=2.1 Hz), 5.62 (1H,d, J=2.1. Hz).

Decomposition of 3r. The CCl_3F–acetone-d_6 solution of *3r* from the ^1H NMR experiment above was allowed to warm up to room temperature, resulting in evolution of nitrogen. On the basis of the similarity of the ^1H NMR spectrum to that of 2-*tert*-butyl-1,1-cyclopropanedicarbonitrile,[23] the product was assumed to be nearly pure trans *2,3-di-*tert*-butyl-1,1-cyclopropanedicarbonitrile.* ^1H NMR (CCl_3F–acetone-d_6): δ 1.13 (18H,s), 2.00 (2H,s).

The reaction between 2b *and* 1e. To a solution of *1e* (2.0 g, 7.5 mmol) in ether was added *2b* (0.5 g, 8.9 mmol) and the mixture was left overnight at room temperature in the dark. The product (*3j*) was precipitated from the solution by adding pentane. Yield: 1.7 g (70 %). Anal. $C_{11}H_{17}BrN_2O_4$: C,H. M.p. 88–90 °C (ether–pentane). ^1H NMR ($CDCl_3$): δ 1.68 (3H,d, J=7.1 Hz), 1.88 (6H,s), 2.67 (1H,d, J=7.8 Hz), 3.75 (3H,s), 3.90 (3H,s), 4.85 (1H,2q, J=7.1 Hz, sep. of quartets: 7.8 Hz).

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