Table I. Relative Chemical Shifts and Dipolar Coupling Constants of **1** and **2** (All Values in Hertz)

Compd	$\nu_2 - \nu_3$[a]	$\nu_2 - \nu_7$	$\nu_3 - \nu_7$	D_{23}[a]	D_{24}	D_{25}	D_{34}	D_{27}	D_{37}	$D_{77'}$	Δf[b]	c, mol %[c]
1	0.7	346.5	347.2	−450.4	−51.6	−20.4	−183.6	−50.1	−79.5	1795.0	0.65	16
2	−17.2[d]			−393.5	14.1	36.6	330.1	−48.6	−48.2	455.1	0.63	13
	−21.7[e]			−393.8	14.2	37.2	329.7					
	−17.3[e]			−393.4	14.1	36.5	330.5					
	−11.9[e]			−393.5	14.1	36.5	330.0					

[a] Probable error of parameters <0.8 Hz. [b] Root-mean-square error for calculated and observed line positions. [c] Concentration. [d] Complete analysis. [e] Subspectral analysis.

Table II. r_{ij} Ratios and Orientation Parameters for **1** and **2**

Compd	r_{23}/r_{34}	r_{24}/r_{34}	r_{25}/r_{34}	r_{27}/r_{34}	r_{37}/r_{34}	$r_{77'}/r_{34}$	S_{xx}[a]	S_{yy}[a]	S_{zz}[a]
1	1.028	1.771	2.081	1.669	2.214	0.760	0.0233	−0.1003	0.0770
	±0.020	±0.018	±0.028	±0.038	±0.051	±0.013	±0.0001	±0.0061	±0.0061
2	1.024	1.769	2.081	1.741	2.293	0.879	−0.0419	−0.0487	0.0906
	±0.006	±0.006	±0.015	±0.028	±0.030	±0.055	±0.0001	±0.0021	±0.0021
Benzene	1.000	1.732	2.000						

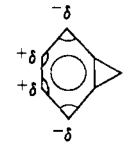
[a] Based on an assumed H_3–H_4 distance of 2.48 A.

been analyzed separately. The results for both compounds are collected in Table I.

Orientation parameters S_{kl} and the ratios of the various H,H, H,F, and F,F distances r_{ij} were then calculated from the experimental data of Table I using an iterative procedure.[9] Since both compounds possess C_{2v} symmetry,[10] two independent parameters are sufficient to characterize their orientation. For these calculations, the distance H_3–H_4 was held constant. The r_{ij} ratios are insensitive to this limitation.[1] To check the results obtained in this way, the ratios of the H,H distances in the six-membered ring of **1** and **2** have also been derived from explicit expressions given for the oriented AA′BB′ system.[11] They were identical with those found by the iterative method. The results, together with the orientation parameters and the relevant r_{ij} ratios of benzene, are presented in Table II. From these values those based on H,F- and F,F-coupling constants in **2**, *i.e.*, r_{27}/r_{34}, r_{37}/r_{34}, and $r_{77'}/r_{34}$, are less reliable, since the experimental D_{HF} and D_{FF} values contain unknown contributions from the anisotropy of the indirect spin-spin coupling.[12]

From the negative signs of the dipolar coupling constants it follows that **1**, as other aromatics,[1] orients with its *x,z* plane preferentially parallel to the external magnetic field. For **2**, however, a different orientation is indicated by the positive sign found for D_{24}, D_{34}, and D_{25} and, more directly, by the different S_{xx} value. In contrast to **1**, the *y* as well as the *x* axis of the molecular coordinate system orient preferentially perpendicular to the magnetic field direction.

Within the limits of error, our measurements yield identical proton geometry for the six-membered ring of **1** and **2**. Compared to benzene, all r_{ij}/r_{34} ratios have increased. This seems to indicate that the benzocyclopropene system suffers a distortion of type **3** with positive changes δ for the CCC bond angles at C_3 and C_4 and negative changes for these parameters at C_2 and C_5. Similar angle distortions have been measured for 7,8-dichlorobenzocyclobutene[13] and benzocyclobutene-7,8-dione,[14] where the strain effects should be comparable to those operating in **1** and **2**. Attempts to obtain the "best" carbon skeleton which fits into the geometry determined by the proton positions in both compounds using "molecular mechanics"[15] are at present under way.



3

Acknowledgments. We wish to thank Dr. D. Schäpel and Professor Dr. E. Vogel, Cologne, for samples of **1** and **2**, Professor Dr. P. Diehl, Basel, for a copy of his program LAOCOONOR, and one of the referees for a helpful comment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

---

[9] Details of the method will be given in the full paper.

[10] The magnetic equivalence of X_7 and $X_{7'}$ in **1** and **2** demonstrates C_{2v} symmetry only on the nmr time scale, but it seems reasonable to assume that both compounds are planar.

[11] P. Diehl, C. L. Khetrapal, and U. Lienhard, *Can. J. Chem.*, **46**, 2645 (1968).

[12] H. Spiesecke and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **6**, 287 (1970).

(13) G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, *J. Phys. Chem.*, **72**, 668 (1968).

(14) F. H. Allen and J. Trotter, *J. Chem. Soc. B*, 916 (1970).

(15) F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

Josef Bernd Pawliczek, Harald Günther*
Institut für Organische Chemie, Universität Köln
Cologne, Germany

Pyrolysis of Cyclopropyl Azides. A Route to 1-Azetines[1]

Sir:

Photolytic or pyrolytic decomposition of cyclopropyl azides with ring enlargement or substituent migration presents a potential route to 1-azetines or N-substituted cyclopropylimines. Neither the latter nor 2-alkyl- (or aryl-) 1-azetines have heretofore been reported.[2] In

---

(1) Stereochemistry. LXIII. For the previous paper in this series, see G. L'abbé and A. Hassner, *Angew. Chem.*, **83**, 103 (1971).

(2) The only 1-azetines in the literature have ether or thioether linkages at the 2 position and are obtained from β-lactams. See, for

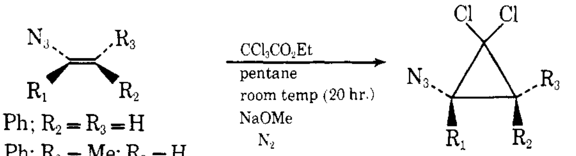
Table I. Yields and Physical Data in the Formation and Pyrolysis of Cyclopropyl Azides **2**

Azide	% yield (isolated)	Nmr spectra, τ^a R$_1$	R$_2$	R$_3$	Bp, °C (mm)	Pyrolysis rate, $k \times 10^{-4}$ sec^{-1}
2a	42	2.60 (s)	7.85, (d, J = 8.0)	8.09 (d, J = 8.0)	83–85 (0.1)	4.6
cis-**2b**	53	2.57 (s)	8.80 (d, J = 6.5)	7.99 (q, J = 6.5)	90 (0.2)	14.7
cis-**2c**	25	8.50 (s)	8.81 (d, J = 6.5)	8.30 (q, J = 6.5)	64 (7)	8.2
trans-**2d**	66	2.57 (s)	7.89 (q, J = 6.5)	8.60 (d, J = 6.5)	82 (0.1)	2.9
trans-**2e**	52	8.27 (s)	8.61 (q, J = 4.5)	8.80 (d, J = 4.5)	65 (7)	1.8

[a] s = singlet, d = doublet, q = quartet; J values in hertz.

fact, since cyclopropyl halides are neither readily susceptible to displacement reactions nor to solvolysis without rearrangement, cyclopropyl azides have remained a virtually unknown class of compounds.[3]

Our recent discovery of a general synthesis of vinyl azides from olefins[4] suggested their reaction with dichlorocarbene as a route to **2**. *N*-Octyl azide has been reported to react with dichlorocarbene to give the corresponding isocyanide dichloride.[5] In sharp contrast, the vinyl azides **1** gave solely the corresponding 1-azido-2,2-dichlorocyclopropanes **2** in moderate yields (see Table I). This is in analogy with recent studies which showed that vinyl azides react at carbon with other electrophiles such as acid[6] and bromine.[7] In a typical experiment 21.9 g (0.115 mol) of ethyl trichloroacetate was added dropwise over a period of 30 min to a solution of 0.1 mol of the vinyl azide and 12.8 g (0.2 mol) of sodium methoxide in 100 ml of pentane at 0° under nitrogen. After stirring for 20 hr at room temperature the mixture was filtered through Celite. Removal of the pentane *in vacuo* left an oil containing starting material and azide. Purification of the latter was accomplished by careful chromatography followed by distillation below 100° at reduced pressure. (*Caution:* these compounds explode on heating at *ca.* 110°.)



1a, R$_1$ = Ph; R$_2$ = R$_3$ = H
b, R$_1$ = Ph; R$_2$ = Me; R$_3$ = H
c, R$_1$ = Me; R$_2$ = Me; R$_3$ = H
d, R$_1$ = Ph; R$_2$ = H; R$_3$ = Me
e, R$_1$ = Me; R$_2$ = H; R$_3$ = Me

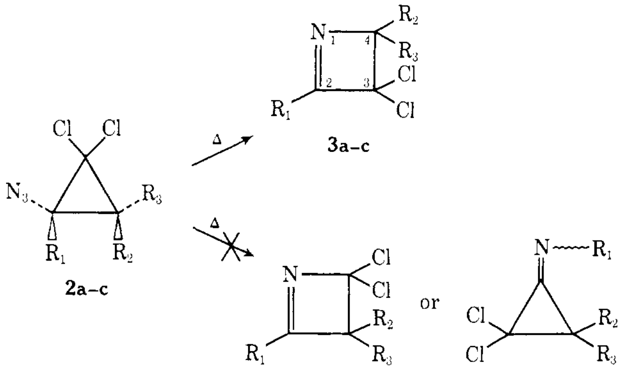
2a–e

Azides **2a–c** decompose smoothly between 105 and 125° in a highly regiospecific[8] manner to give the corresponding 3,3-dichloroazetines **3** in 50–75% isolated yields (see Table II). No spectral evidence for formation of **4** or **5** was observed. The primary side products appear to be the nitrile **6** and the olefin **7** (*ca.* 5%), possibly resulting from the fragmentation of the azetine ring. Typically, 5 g of the azide was refluxed in 200 ml of toluene for 9 hr, the toluene removed *in vacuo*, and the resultant azetine chromatographed on silica gel.

Table II. Yields and Nmr Data of Azetines **3**

Azetine	% yield	Nmr spectra, τ^a
3a	55	5.49 (s, 2 H) 2.51, 2.05 (2 m, 5 H)
3b	72	8.49 (d, 3 H, J = 7) 5.40 (q, 1 H, J = 71) 2.60, 2.03 (2 m, 5 H)
3c	75	8.59 (d, 3 H, J = 6.5) 7.91 (d, 3 H, J = 1.6) 5.56 (q of q, 1 H, J = 1.6 and 6.5)

[a] s = singlet, d = doublet, q = quartet, m = multiplet; J values in hertz.

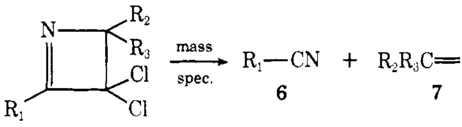


3a–c

2a–c

4

5



3 **6** **7**

The structures of **3a–c** were indicated by ir, nmr, and mass spectra. The mass spectra showed strong peaks corresponding to the molecular ion, the nitriles **6**, and the olefins **7**. Conclusive evidence for the structures came from acid hydrolysis and LiAlH$_4$ reduction to give the analogous β-amino-α,α-dichloroketones **8** and azetidines **9**, respectively.

The structures of the amino ketones **8a–c** were indicated by spectral data, the mass spectra being especially helpful since they showed the expected amine α cleavage corresponding to R$_2$R$_3$C═NH$_2^+$ and no α cleavage at *m/e* 98, 100, and 102, corresponding to CCl$_2$═NH$_2^+$. The crude nmr spectra of **8a–c** indicated

---

example, G. Pifferi, P. Consonni, G. Pelizza, and E. Testa, *J. Heterocycl. Chem.*, **4**, 619 (1967); D. Bormann, *Justus Liebigs Ann. Chem.*, **752**, 124 (1969). For another recent example, see A. Hassner, J. O. Currie, A. S. Steinfeld, and R. F. Atkinson, *Angew. Chem., Int. Ed. Engl.*, **9**, 731 (1970).

(3) Cyclopropyl azide itself has been reported by W. Kirmse and H. Schutte, *J. Amer. Chem. Soc.*, **89**, 1284 (1967), and W. Kirmse and H. Schutte, *Chem. Ber.*, **101**, 1674 (1968).

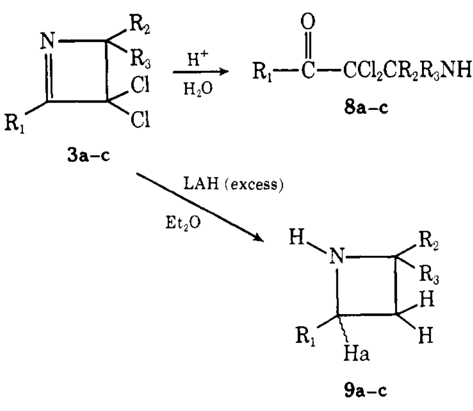
(4) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); A. Hassner, *Accounts Chem. Res.*, **4**, 9 (1971).

(5) J. E. Baldwin, *Chem. Commun.*, 968 (1968).

(6) H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, **92**, 1675 (1970); A. Hassner, E. S. Ferdinandi, and R. J. Isbister, *ibid.*, **92**, 1672 (1970).

(7) A. Hassner and A. B. Levy, *ibid.*, in press.

(8) Regio is used to describe a directional preference in bond making or breaking: A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).



no other products present. The structures of azetidines **9a–c** were obvious from their ir, nmr, and mass spectra. That the geminal hydrogens were in the 3 position in **9a** and **b** was indicated by the low-field (τ 5.4) broad triplet for H_a. In **9c** H_a could not be resolved, but the mass spectra showed the expected α cleavage at *m/e* 43 ($CH_3CH{=}NH\cdot^+$) and no peak at *m/e* 30 ($CH_2{=}NH\cdot^+$).

The regioselectivity in the formation of **3** over **4** and **5** cannot be equated with conformational effects[9] governing a concerted loss of N_2 with ring enlargement, since the conformers of **2** are expected to be of nearly equal stability and should produce a mixture of **3**, **4**, and **5**.

The driving force for ring expansion in preference to formation of a cyclopropylimine **5** (Ph migration) must be relief of ring strain in going from a three- to a four-membered ring. Apparently, the reaction involves selective migration of the electron richer CH_2 (or CR_2) rather than the CCl_2 ring residue to the electron-deficient nitrogen atom.

Rate data on the pyrolysis of cyclopropyl azides **2** (Table I) indicate that in general cis substituents (see **2b** and **2c**) accelerate the reaction. This implies that the rate-determining step cannot be loss of N_2 unless the reaction is concerted. A concerted ring expansion with loss of nitrogen is in fact suggested by the negative entropy of activation ($\Delta S^{\ddagger} = -18$ eu for **2c** → **3c**) and is in accord with data on pyrolysis of simple alkyl azides.[10]

Acknowledgment. Support of this work by a grant (CA 04474) from the National Cancer Institute (Public Health Service) is gratefully acknowledged.

---

[9] Different migratory aptitudes in the photolysis of organic azides have been ascribed to ground-state conformational preferences; see R. M. Moriarty and R. C. Reardon, *Tetrahedron*, **26**, 1379 (1970).

[10] W. Lwowski, "Nitrenes," Interscience, New York, N. Y., 1970, Chapters 3 and 4.

[11] NIH Predoctoral Fellow, 1968–1971.

A. B. Levy,[11] A. Hassner*
Department of Chemistry, University of Colorado
Boulder, Colorado 80302

Received December 5, 1970

Effect of CH Scalar Coupling on ^{13}C Transverse Relaxation Times

Sir:

In view of the increasing interest in ^{13}C nmr spectroscopy, we wish to report some preliminary relaxation studies of ^{13}C-enriched compounds. We find that the transverse relaxation times, T_{2C} ($\equiv R_{2C}^{-1}$), are usually shorter than the longitudinal relaxation times, T_{1C} ($\equiv R_{1C}^{-1}$). This result influences the sensitivity and resolution in both conventional and Fourier transform (FT) ^{13}C spectra and, in particular, affects the signal enhancement obtainable by the use of refocusing schemes such as driven equilibrium and spin–echo Fourier transform (DEFT and SEFT) techniques.[1–3]

The T_{2C} measurements were performed at 15.08 MHz by the usual Meiboom–Gill[4]-modified Carr–Purcell[5] technique on a high-resolution magnet with external fluorine lock. The π pulse width was 6 μsec and the inhomogeneity over the sample gave a free-induction decay constant $T_2^* \sim 100$ msec. Degassed and sealed sample tubes were constricted below the liquid surface to minimize interchange between liquid and vapor. T_{1C} and T_{1H} values were measured by π–τ–$\pi/2$ pulse sequences, T_{1C}'s at 15.08 MHz, T_{1H}'s at 23.2 MHz. The T_1 and T_2 values were obtained by the usual least-squares fitting procedures.

Table I shows that T_{2C} is substantially shorter than T_{1C}[6] for methyl iodide and methyl-d_3 acetate-^{13}C. We would like to point out that short T_{2C}'s occur when relaxing spin-$^1/_2$ nuclei, *e.g.*, protons, are coupled to ^{13}C such that

Table I. Relaxation Times[a] for 60% ^{13}C-Enriched Compounds at 25°

	T_{1C}, sec	T_{2C}, sec	T_{1H},[b] sec
$^{13}CH_3I$	13.4	3.9	10.9[c]
$^{13}CH_3COOCD_3$[d]	19.2	6.1	12.5
$^{13}CS_2$	48[e]	38	

[a] The experimental error is estimated to be ~5%. [b] T_{1H} for 100% enriched compounds will be less than these values. [c] T_{1H} for $^{12}CH_3I$ at 25° is reported [M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, **69**, 659 (1965)] to be 12.5 sec. [d] Deuterium enrichment is 99%. [e] T_{1C} = 30 sec (15 MHz, 26–28°) was measured by rapid adiabatic passage: A. Olivson, E. Lippmaa, and J. Past, *Eesti NSV Tead. Akad. Toim.*, **16** 390 (1967).

$$A \equiv 2\pi J \gg R_{1H} \qquad (1)$$

where $R_{1H} \equiv 1/T_{1H}$. Gutowsky, Vold, and Wells[8] have pointed out the analogy between chemically exchanging, equally populated, uncoupled two-site systems and relaxing, scalar-coupled AX systems. They suggest that the two cases are related by the simple substitution of $\Omega \rightarrow A/2$ and $k \rightarrow R_{1X}$, where Ω is half the chemical shift between the two sites, k the exchange rate, and R_{1X} the spin–lattice relaxation rate of X.

Scalar contributions to R_{2A} for a general AX_n system originate from relaxation processes within the X manifold which preserve the spin state of A while changing the scalar coupling energy by a nonzero multiple of J. These processes randomly alter the precession frequency

---

[1] E. D. Becker, J. A. Ferretti, and T. C. Farrar, *J. Amer. Chem. Soc.*, **91**, 7784 (1969).

[2] A. Allerhand, *ibid.*, **92**, 4482 (1970).

[3] J. S. Waugh, *J. Mol. Spectrosc.*, **35**, 298 (1970).

[4] S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29**, 688 (1958).

[5] H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).

[6] We realize that T_1 is not rigorously defined for strongly coupled AX_n systems (see, *e.g.*, ref 7, p 295) but we could detect no deviation from exponential behavior.

[7] A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 311.

[8] H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, **43**, 4107 (1965).