Pergamon

Tetrahedron 55 (1999) 12783–12796

TETRAHEDRON

Thiocarbonyl Ylides and Electrophilic Azo Compounds; Sterically Hindered Cyclic Hydrazodicarboxylic Esters [1]

Rolf Huisgen,* Xingya Li, Grzegorz Mloston,[2] Rudolf Knorr, Helmut Huber, and David S. Stephenson

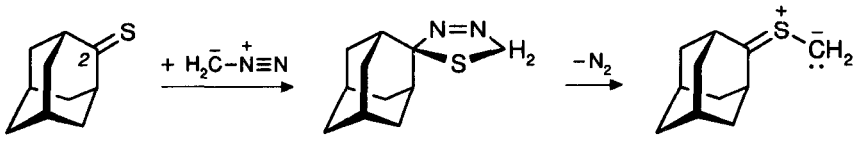
Institut für Organische Chemie der Universität München
Butenandtstr. 13, D-81377 München

Received 30 August 1999; accepted 3 September 1999

Abstract: The cycloadduct **5**, prepared from adamantanethione *S*-methylide with dimethyl azodicarboxylate, exists in solution in two conformations **P** and **Q** (70:30 in $CDCl_3$), which are separated by a barrier of $\Delta G^{\ddagger}$ 18.3 ± 0.6 kcal mol^{-1}; according to NMR spectra, both forms are chiral. Steric hindrance to 3'N – CO_2CH_3 rotation by the adamantane system generates *C=O outside* and *C=O inside* conformations. The barrier to enantiomerization (AB → A_2 for 5'-H_2) is higher (> 20.1 kcal mol^{-1}). Three combinations of rate processes are discussed. Except for the 5'-methyl compound **19a**, the chiral cycloadducts of four other thiocarbonyl ylides to dimethyl azodicarboxylate do not show diastereoisomeric conformations in their NMR spectra at ambient temperature.

Adamantanethione S-Methylide

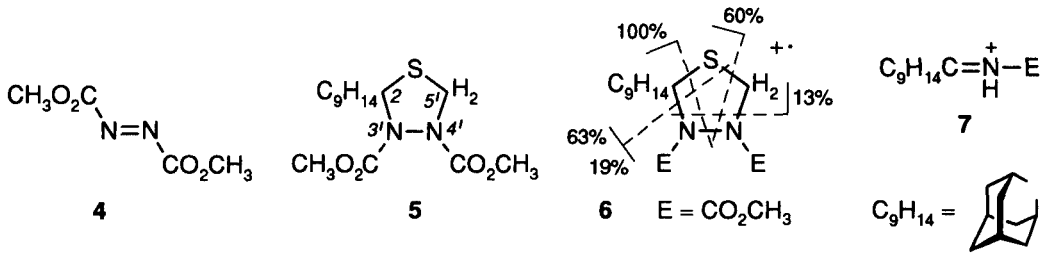
The readily available 2,5'-dihydrospiro[adamantane-2,2'-(1,3,4)-thiadiazole] (**2**) eliminates N_2 at 40°C in THF with a half-reaction time of 90 min.[3] The nucleophilic 1,3-dipole **3** undergoes [3+2] cycloadditions with electrophilic multiple bonds: Ethylene and acetylene derivatives with electron-attracting substituents,[4] thiocarbonyl compounds, aldehydes, and imines.[5]



1 **2** **3**

N-Acylazo compounds are strong electrophilic reagents. After heating of **2** with 1.05 equiv of dimethyl azodicarboxylate (**4**) for 8 h at 40°C, ^{1}H NMR analysis indicated 90% of **5**. In the MS of the thiadiazolidine derivative **5**, the molecular peak appears with 99% intensity, and scheme **6** discloses four fragmentation pathways. The molecular formulae of the fragments were confirmed by the intensities of ^{13}C and (^{34}S+$^{13}C_2$) isotope peaks. The base peak, *m/z* 208, is devoid of sulfur and corresponds to $C_{12}H_{18}NO_2^+$; it would fit the iminium formula **7** or an isomeric structure. $C_{12}H_{17}NO_2S^+$ for *m/z* 239 (60%) results from another cleavage and is in accord with [M^+- H_2C=N-CO_2CH_3]. The splitting of M^+ along the line of the original cycloaddition is of minor importance: *m/z* 180 (13%) for the radical cation of **3**.

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00790-5



Hindered Rotation in the Adduct 5 of Dimethyl Azodicarboxylate

If the two carbamic ester groups were regarded as *quasi*-coplanar, **5** should have C_s symmetry, and a reduced set of ^{13}C signals for the adamantane C-atoms would be anticipated: three CH_2 (2:2:1), three CH (2:1:1), and the quaternary C-2. In contrast, the ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 25°C) of the pure **5** indicates a 70:30 mixture of two conformers, **P** and **Q**, both of which display ten different ^{13}C signals for the adamantane part, thus revealing *chirality*: five CH_2 and four CH signals at δ 26 - 38, and the C-2 at δ 89.5 (**P**) and 89.1 (**Q**). The resonances of C-2 and C-5' are shifted to higher frequencies by S and N functions. The C-atoms of C=O and OCH_3 occur likewise in pairs with height ratios of 70:30.

In the ^1H NMR spectrum (400 MHz, $CDCl_3$, 25°C) of **5**, two AB patterns for 5'-H_2 (δ 4.41, 4.93 for **P** and 4.49, 4.80 for **Q**) confirm the ratio of 70:30 for the slowly equilibrating forms. **P**/**Q** = 68:32 in Cl_2CD-$CDCl_2$ and 66:34 in $C_6D_5NO_2$ show a small influence of the solvent. The *gem*-coupling constant of 5'-H_2, ^2J = 7.8 - 8.1 Hz, is diminished by the proximity of two heteroatoms.[6] Two ester methyl singlets each for **P** and **Q** appear in the narrow range of δ 3.65 - 3.80.

Before the hindered rotation is discussed in the light of previous evidence, the temperature dependence of the NMR spectra will be considered. *At 25°C*, sharp ^{13}C signals demonstrate slow interconversion of **P** and **Q** and allow an unambiguous pairwise ordering. The ^{13}C resonances *at 50°C* disclose various stages of line broadening and coalescence. *At 120°C* (Cl_2CD-$CDCl_2$) the equilibration is fast, and *one* set of ten adamantane signals establishes that *chirality is retained.*

According to 400 MHz ^1H NMR spectra, coalescence of corresponding OCH_3 singlets of **P** and **Q** was observed at 40-65°C in three solvents. In $C_6D_5NO_2$, $\Delta\nu$ 8.1 and 14.5 Hz were found for the two OCH_3 pairs at 25°C, but T_C 65°C resulted for both pairs as a consequence of different temperature dependencies of $\Delta\nu$; in Fig. 1 the asymmetry of band shapes is noticeable. All changes from 25° - 150°C were found to be fully reversible. On cooling of the $CDCl_3$ solution to -50°C, some line broadening, but no further splitting of the ^1H resonances was observed.

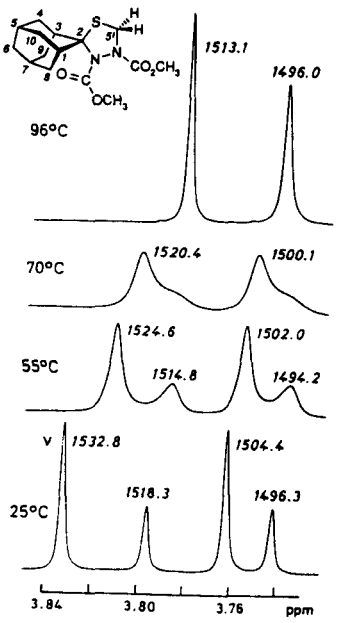


Figure 1. Coalescence in the ^1H NMR spectra ($C_6D_5NO_2$, 400 MHz) for the OCH_3 singlets of conformations **P** and **Q** of **5**.

The AB spectra of 5'-H_2 for **P** and **Q** enter coalescence, in the A and B part separately, with T_C 68° - 96°C (Table 2), until *one* AB spectrum remains at higher temperatures; the doublet signals are not separated at the basis. Heating to 120°C (Cl_2CD-$CDCl_2$) and 150°C ($C_6D_5NO_2$) is accompanied by further signal broadening, but coalescence for AB → A_2 is still not reached.

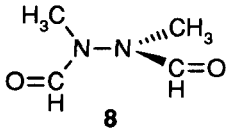
Applying the band shape equation for unequal concentrations of equilibrium partners,[7,8] nine values of T_C and $\Delta\nu$ for the merging of **P** and **Q** allowed the determination of nine values of k_C and hence $\Delta G_C^{\ddagger}$. $\Delta G_P^{\ddagger}$ and $\Delta G_Q^{\ddagger}$ differ by the free equilibrium enthalpy. The evaluated $\Delta G_P^{\ddagger}$ ranges from 17.7 to 18.7 kcal mol^{-1} with 18.3 ± 0.6 kcal mol^{-1} as averaged value (Table 2). No distinct solvent influence was observed. The T_C of the next dynamic process, which should make the diastereotopic 5'-H_2 enantiotopic (AB → A_2), must be significantly above 150°C; $\Delta G^{\ddagger} > 20.1$ kcal mol^{-1} was calculated for 150°C by the expression for the coalescence AB → A_2.[9]

Discussion

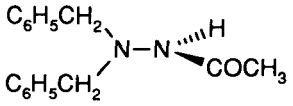
Electron diffraction data of hydrazine (gas) reveal a dihedral angle of 91(2)° between the lone-pair orbitals.[10] *Ab initio* calculations also favor a nearly orthogonal arrangement rather than *trans*-located n-orbitals; at STO-4LGF level, Θ = 95° was obtained for the energy minimum, and rotational barriers of 10.8 and 4.2 kcal mol^{-1} resulted for Θ = 0° (n-orbitals eclipsed) and 180°, respectively.[11]

The interplay of N inversion and N – N rotation in substituted hydrazines has been a much studied problem.[12] The resonance effect resulting from N-acylation tends to planarize the nitrogen bond system. 1,2-Diformylhydrazine has a planar conformation with Θ = 180°, due to the presence of two intramolecular hydrogen bonds (X-ray,[13] neutron diffraction [14]). In 1,2-diformyl-1,2-dimethylhydrazine (**8**), two planar *N*-methylformamide units are orthogonally arranged (Θ = 91.2°),[15] revealing the same conformational preference as hydrazine itself.

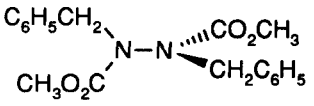
The topomerization of the benzyl protons in the *N*-acetylhydrazine **9** requires N – N rotation *via* a barrier of $\Delta G_{341}^{\ddagger}$ 15.5 kcal mol^{-1}.[16] A rotational barrier of 23.5 kcal mol^{-1} (T_C 192°C) was reported for the hydrazodicarboxylate **10**.[17] We must conclude that N-acylation *decreases* the N inversion barrier, but *increases* the barrier to N – N rotation; this is an unexpected effect since the delocalization of the unshared electron pair should diminish the repulsion of the n-orbitals. *Non-bonded interaction* between the carbamate groups was invoked to explain the high rotational barriers of hydrazodicarboxylates.[17,18b]



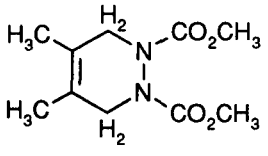
8



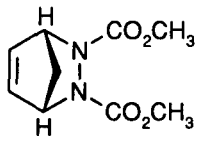
9



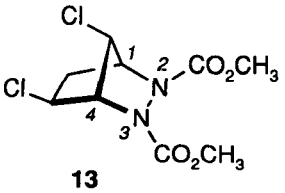
10



11



12



13

In now classic papers, the research groups of Lehn [18] and Sutherland [19] studied the temperature dependence of the ^1H NMR spectra of cyclic hydrazodicarboxylates and observed *two* dynamic processes; *e.g.*, for **11** barriers of $\Delta G^{\ddagger}$ 20.7 and 14.7 kcal mol^{-1} were determined.[19b] The higher one was attributed to ring inversion, also called "bridge flipping"; Anderson and Lehn supposed the passing of a *quasi*-coplanar transition state (TS) of the two carbamic ester groups by twisting about the N–N bond.[18b] At lower temperature, the number of ester alkyl signals increased; the authors assumed that it is the rotation about the N–CO_2CH_3 bond ($\Delta G^{\ddagger}$ 14.7 kcal mol^{-1} at -3°C) which becomes frozen.

As long as the carbamate group was regarded as nearly planar,[18b] the bicyclic diester **12** with its rigid 5-membered ring should approach the *quasi*-coplanar TS for the ring inversion of **11**.[12a] Due to the raising of the ground state of **12**, the ^1H NMR spectrum did not disclose a torsional barrier of the N–N bond. The barrier to rotation of N–CO_2CH_3 (13.9 kcal mol^{-1} at -5°C) was similar to that observed for **11**.[18c,19b]

The group of Sutherland presumed that the N atoms of the bicyclic **12** are somewhat pyramidal.[19b] A confirmation came from a later X-ray analysis of **13** by Offereins et al.[20] The two planar ester groups are located *exo* and *endo* at the bicyclic system; the dihedral angle at C1-N2–N3-C4 is only 0.4°, but that of OC-N2–N3-CO amounts to about 90°. Nelsen recommended α(av), a third of the angle sum at the N atom, as a measure of pyramidality (120° for planar-trigonal, 109.5° for tetrahedral).[12b] Values of α(av) = 113.9 (N2) and 113.2° (N3) for **13** indicate substantial pyramidality. Obviously, the repulsive force between *cis*-coplanar amide groups was previously underestimated; in addition, the strain of the rigid 5-membered ring favors pyramidalization. The bicyclo[2.2.1]heptane system does not allow much freedom to the angle C1-C2-C3: 103-104° in norbornane [21,22] and norbornene.[23] Bond angle C1-N2-N3 is 105° in **13**.[20]

We are not aware of data on structures and inversion barriers of *monocyclic 5-membered* hydrazodicarboxylates. The 5-membered ring in **5** is more flexible than that in the bicyclic **12** or **13** and can accommodate somewhat larger bond angles, *i.e.*, N hybridizations between sp^3 and sp^2, with less strain energy.

Regrettably, we did not so far obtain suitable monocrystals of **5** for X-ray diffraction. According to molecular models, the adamantane system enforces twisting of the 3'N–CO_2CH_3 of **5**, thus decreasing the carbamate resonance and increasing the pyramidalization at 3'N. A substantial barrier separating a *C=O outside* and *C=O inside* conformation is anticipated. The energy maximum in the rotational profile of RR'N–CO_2CH_3 of **12** (13.9 kcal mol^{-1}) occurs at 90°, and the minimum near planarity. However, for 3'N–CO_2CH_3 rotation of **5**, the maximum should be close to 0° where the van der Waals pressure in the collision with the voluminous adamantane group is greatest, but the gain in carbamate resonance provides partial compensation. At the minimum, the carbamate conjugation is strongly disturbed.

An AM1 calculation of **5** confirms *C=O outside* and *C=O inside* conformations – the first is by nearly 2 kcal mol^{-1} better than the second – as minima on the potential surface (Fig. 2).[24] Additional minima are generated by two nearly planar conformations of 4'N–CO_2CH_3; the slighly better one is illustrated in Fig. 2. The heteroring is recognized as an envelope conformation with C2 as the flap, thus diminishing the van der Waals pressure. The distance from carbonyl oxygen (3'N-CO_2CH_3) to the closest nonbonded neighbor, the 4-H of adamantyl, is 2.18 Å (**5A**) and 2.15 Å (**5B**).

Both N atoms are pyramidalized, N3' stronger than N4', as shown for **5A** by α(av) = 111.9° and 116.9°, respectively. In the *outside* form **5A** (*inside* form **5B**), the O=C–O plane cuts the plane C2-N3'-C(O) at an angle of 81° (79°); thus, the conjugation 3'N–CO is virtually extinct. As for 4'N–CO_2CH_3, the interplanar angle between C5'-N4'-C(O) and O=C–O amounts to 9° (**5A**) and 7° (**5B**), asserting conjugative coupling. We will abstain from further numerical evaluation since the weakness

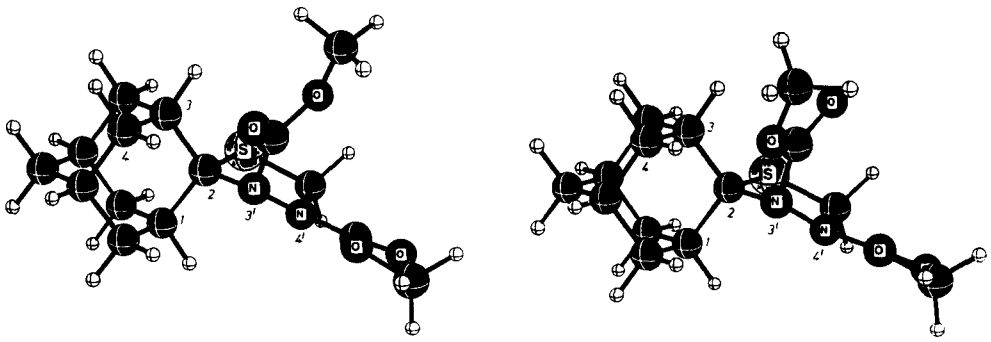


Figure 2. *C=O outside* (**5A**, left) and *C=O inside* conformation (**5B**, right) calculated by AM1.

of the semiempirical AM1 in reproducing diacylhydrazine structures is well-known;[25] also the basis set for sulfur bonding is unsatisfactory.

What is the nature of the barrier (18.3 kcal mol^{-1}) separating **P** from **Q** (70:30) ? Why does the high-temperature NMR spectrum still indicate chirality ? Three possibilities will be discussed.

Model 1. The chiral forms **P** and **Q**, observed in the NMR spectra, correspond to **5A** and **5B**. The 18.3 kcal mol^{-1} barrier belongs to the rotation of $3'N-CO_2CH_3$ which interconverts **5A** and **5B**. The higher barrier of > 20.1 kcal mol^{-1} (T_C above 150°C) is ascribed to the ring inversion by N – N torsion; this enantiomerization will change the AB spectrum of $5'\text{-}H_2$ into A_2.

At first glance, a significantly lower inversion barrier would be expected for the 5-membered ring of **5** than for the 6-membered of **11**, hydrogenated at the double bond (19.4 kcal mol^{-1}).[18d] The comparison of the inversion barrier of the cyclohexane chair ($\Delta H^{\ddagger}$ 10.7 kcal mol^{-1}) with the "conformational flux" of the cyclopentane envelope (2.8 kcal mol^{-1} for pseudorotation) [26] is pertinent. Assuming that the N – N twisting consists essentially of two consecutive N inversions, the loss of carbamate resonance at $3'N-CO_2CH_3$ is a destabilization of the ground state and should facilitate the process. On the other hand, it is difficult to estimate the hindrance to the N inversion by the adamantane system. Barriers to N – N rotation in hydrazodicarboxylic esters with 6-membered ring are sensitive to small structural changes,[12] but systems with strong steric interference on *one* side have not been studied.

Model 2. The lower barrier (18.3 kcal mol^{-1}) is due to N – N torsion and the higher is attributed to the $3'N-CO_2CH_3$ rotation. The N – N torsion exchanges *C=O outside* and *C=O inside* conformations. The single molecule undergoes a diastereoisomerization leading from **5A** to the enantiomer of **5B** and *vice versa*. The equilibrating pairs,

$$(R)\text{-}\mathbf{P} \rightleftharpoons (S)\text{-}\mathbf{Q} \quad \text{and} \quad (S)\text{-}\mathbf{P} \rightleftharpoons (R)\text{-}\mathbf{Q},$$

occur as 50:50 mixture, but chirality is retained. It is the $3'N-CO_2CH_3$ rotation which finally generates *quasi* symmetry at high temperature. The changed barrier assignments relieve some of the flaws of *model 1* and offer higher consistency.

However, we have neglected so far rotamers of $4'N-CO_2CH_3$ as a further stereoelement. For the rotation of $(CH_3)_2N-CO_2CH_2C_6H_5$, $\Delta G^{\ddagger}$ 15.9 kcal mol^{-1} at 17°C was measured,[19a] and values of 12.6 - 16.0 kcal mol^{-1} have been reported for $N-CO_2R$ rotation of various 6-membered cyclic hydrazodicarboxylic esters.[12b] As mentioned, the ^1H NMR signals of **5** show some line broadening on cooling to -50°C, but

no further splitting. It is uncertain, whether extreme equilibrium concentrations or small differences of chemical shifts ($\Delta\nu$) can be responsible for the non-occurrence.

Model 3. The two stable conformations of 4'N – CO_2CH_3 are both conjugated, but still slightly pyramidal at nitrogen; they occur 70:30 and are ascribed to **P** and **Q**. When their interconversion barrier is 18.3 kcal mol^{-1}, then the equilibration of the *C=O outside* and *C=O inside* conformations - **5A** with the enantiomer of **5B** and *vice versa* - must be fast on the NMR time scale, down to -50°C. This third solution of our DNMR problem would require increasing barriers: N – N torsion < 4'N – CO_2CH_3 rotation (18.3 kcal mol^{-1}) < 3'N – CO_2CH_3 rotation (enantiomerization). However, no statement about the ratio of **5A** and **5B** is feasible. With an energy difference of ~ 2 kcal mol^{-1} (AM1 calculation), the second form may not become visible in the NMR spectra.

The more flexible heterocycle in **5** has a lower ring strain than **12**. On the other hand, the loss of carbamate resonance in the twisted 3'N – CO_2CH_3 of **5** raises the energy of the ground state. It is conceivable for the process *(R)*-**5A** $\rightleftharpoons$ *(S)*-**5B** that the ester group glides along the surface of the adamantane sphere without N – CO_2CH_3 rotation. Taking the low pseudorotation energies of the 5-membered ring into account, the N – N torsion might well be the fastest of the three motions in **5**.

It may be recalled that only *one* dynamic process was found in the NMR spectra of **12** and related compounds, and there is good reason to attribute the barrier of 13.9 kcal mol^{-1} to N – CO_2CH_3 rotation.[18,19] However, none of the rotational barriers, described for N – CO_2R above, reached 18.3 kcal mol^{-1}, discussed here for 4N' – CO_2CH_3; we do not see an obvious reason for the increase.

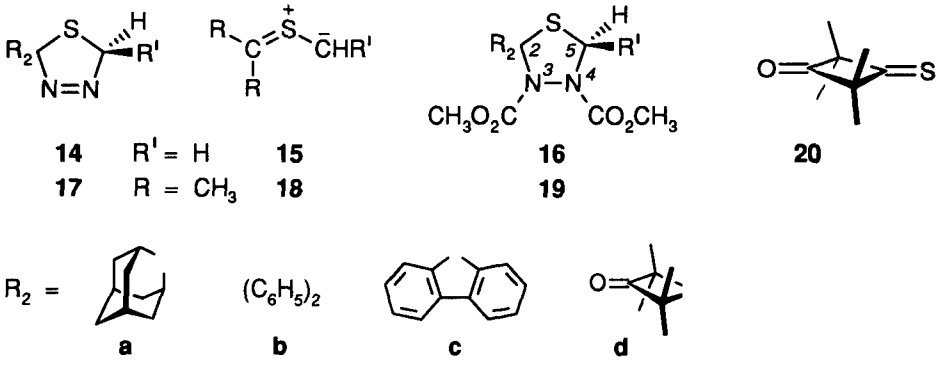
None of the three interpretations of the DNMR phenomena of **5** is fully satisfying; presently, we leave the decision between *models 2* and *3* open. More data on 5-membered cyclic hydrazodicarboxylic esters are desirable. Admittedly, not all the energy values reported for the 6-membered cyclic bis-carbamates [12] fit a consistent pattern either.

Cycloadducts of Further Thiocarbonyl Ylides with Dimethyl Azodicarboxylate

For the preparation of the 5'-methyl compound **17a**, diazoethane was added to adamantanethione (**1**). Whereas diazomethane and **1** furnish both the 1,3,4- and the 1,2,3-thiadiazoline, depending on solvent polarity,[3,27] the reaction with diazoethane provided 93% of the crystalline 1,3,4-thiadiazoline **17a**; there was no evidence for the occurrence of the regioisomer, as also noticed by Katada *et al.*[28] The N_2 elimination in toluene at 81°C proceeds with $t_{1/2}$ 2.6 min; the 5'-methyl slows down the rate, measured for **2**,[3] by a factor of 2.8. The N_2 extrusion from **17a** in the presence of 1.1 equiv of **4** furnished 93% of cycloadduct **19a**.

The ^{13}C NMR spectrum of **19a** ($CDCl_3$, 25°C, 100 MHz) shows a double set of ten adamantane signals, as described above for the ^{13}C parameters of **5**. With 72:28 even the ratio of conformations **P** and **Q** is similar as that observed for **5**. C-5' and 5'-CH_3 as well as the carbonyl and methoxy groups of 3'-CO_2CH_3 and 4'-CO_2CH_3 appear likewise in doubled signals. The ^1H NMR spectrum confirms the presence of only two chiral conformations **P** and **Q**; *e.g.*, two quartets for 5'-H, two doublets for 5-CH_3, and four ester methyl signals appeared.

C-5' is an additional stereocenter in the **19a**, but no further increase of conformers was observed. It cannot be excluded, that the signals of further conformations, **P'** and **Q'**, remain below the analytical limit. No extra signals appeared. That poses a tough problem to interpretations by *models 1-3*. Conceivably, eclipsing effects by 5'-CH_3 curb the populations of various conformers. A detailed discussion should be postponed until the temperature dependence of the NMR spectra has been studied.



14 R' = H **15** **16** **20**
17 R = CH_3 **18** **19**

R_2 = **a** $(C_6H_5)_2$ **b** **c** **d**

Dimethyl azodicarboxylate was reacted with four more thiocarbonyl ylides, **15b,c,d** and **18d**. The crystalline cycloadducts (Table 1) **16b,c,d** show in their NMR spectra only *one* AB pattern for diastereotopic 5'-H_2 at room temperature. All the groups R_2 = **a** - **d** will exert steric hindrance to the $3N-CO_2CH_3$ rotation.

Table 1. Cycloadducts of thiocarbonyl ylides with dimethyl azodicarboxylate

1,3,4-Thiadiazolidine			NMR Parameters ($CDCl_3$, 25°C)				
Formula	%Yield	mp (°C)	δ_C(C-5')		δ_H (ppm)		
5	93	112-113	**P** 48.70	5'-H_2	4.41,	4.93	
			Q 48.76		4.49,	4.80	
19a	93	87-89	**P** 60.99	5'-H	5.44	5'-CH_3	1.50
			Q 61.04		5.33		1.48
16b	72	98-100		5-H_2	4.63,	5.13	
16c	88	169-171	52.3	5'-H_2	4.86,	5.50	
16d	58	110-112		5'-H_2	4.38,	4.58	
19d	63	117-119		5'-H	5.22	5'-CH_3	1.52

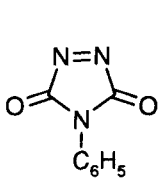
The 5'-methyl-1,3,4-thiadiazoline **17d** was prepared from **20** with diazoethane and converted to the cycloadduct **19d** as usual. The ^1H NMR spectrum of **19d** displays *one* AX_3 spectrum, due to 5'-H(CH_3).

Thus, the occurrence of equilibrating diastereoisomers appears to be a unique feature of the adamantane series, for which we have no good argument. Among the three interpretations, proposed above, ***model 3*** faces the greatest difficulties. Why should the distant R_2 influence either the ratio of the two conjugated conformations of $4'N-CO_2CH_3$ or their rate of equilibration so strongly ? Only further studies can shed light upon the interplay of phenomena.

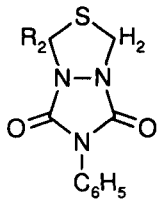
Steric hindrance is an ambiguous term. When rate constants are used for establishing increasing steric demand for a series of groups, the sequence may highly depend on the nature of the reaction considered. ***Size and shape*** of the groups will determine the degree of hindrance. In 1,3-dipolar cycloadditions with thiobenzophenone, adamantanethione (**1**) and thione **20**, the rate ratios vary widely.[29]

4-Phenyl-1,2,4-triazoline-4,5-dione

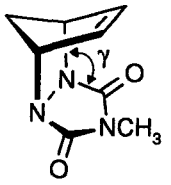
The cyclic diacylazo compound **21** belongs to the most potent dienophiles and dipolarophiles. The in situ cycloadditions of the thiocarbonyl ylides **2** (at 40°C) and **15b** (at -45°C) furnished the triazolidines **22** (55%) and **23** (87%), respectively. A sharp singlet for 5-H_2 was found in both of the ^{1}H NMR spectra.



21



	R_2
22	
23	$(C_6H_5)_2$



24

Several Diels-Alder adducts of **21** with cyclic dienes were subjected to X-ray analysis by Kaftory et al.[30] The diacylimide ring of **24** is close to planar, but γ 128.3° demonstrates the non-planar annulation. The disadvantage of having the lone pairs at the two N atoms in parallel p-orbitals is avoided by strong pyramidalization: α(av) = 110.5° is close to the tetrahedral angle. The strain in the bridged pyrazolidine ring likewise promotes N pyramidality. A dynamic process in a related compound was ascribed to a simultaneous double N inversion ($\Delta G^{\ddagger}$ 8.7 kcal mol^{-1} at -72°C), i.e., the eclipsing interaction of the lone-pair orbitals is retained during the process.[30c]

EXPERIMENTAL

General.[5]

Adamantanethione S-Methylide (3)

Dimethyl Spiro[adamantane-2,2'-(1,3,4)-thiadiazolidine]-3',4'-dicarboxylate (5): (a) *Dimethyl azodicarboxylate* (**4**, 307 mg, 2.10 mmol) and 2.00 mmol of **2** [3] in 5 ml of abs. THF were heated at 40°C for 8 h. After evaporation of the solvent, the residue was dissolved in $CDCl_3$, and a weighed amount of *sym*-tetrachloroethane (δ 5.92) was added. Comparison of the ^{1}H NMR integrals of the two d at δ 4.74 and 4.85 with the s of the standard established 1.80 mmol (90%) of **5**. Recrystallized from ethanol, 370 mg (57%), mp 112-113°C, was obtained. - IR (KBr): $\tilde{\nu}$ 1282 cm^{-1} st (C-O); 1480, 1548 st; 1710, 1747 st (C=O). - ^{1}H NMR (400 MHz, 25°C, isomers **P**/**Q** 70:30): δ 1.6 - 2.0 (m, 10 H), 2.25, 2.20 (2 d br, J = 12.5 Hz, 2 H of **P** and **Q**), 2.55 (appar. t, 1 H), 2.98 (s br, 1 H); **P**: 3.745, 3.762 (2 s, 2 OCH_3), 4.41, 4.93 (AB, J_{gem} = 7.8 Hz, 5'-H_2); **Q**: 3.751, 3.798 (2 s, 2 OCH_3), 4.49, 4.80 (AB, J_{gem} = 7.8 Hz, 5'-H_2). - ^{13}C NMR (100 MHz, DEPT; although unreliable, second decimals are given, because $\Delta\delta$ are often small), Conformer **P**: δ 26.59, 26.66, 35.34, 37.69 (4 CH), 34.03, 35.01, 36.08, 37.51, 37.74 (5 CH_2), 48.70 (C-5'), 53.41, 53.80 (2 OCH_3), 89.54 (C-2), 155.89, 156.45 (2 C=O); Conformer **Q**: δ 26.64, 26.66, 35.38, 37.94 (4 CH), 34.57, 35.12, 36.02, 37.55, 37.79 (5 CH_2), 48.76 (C-5'), 53.39, 53.86 (2 OCH_3), 89.12 (C-2), 154.12, 156.35 (2 C=O); all signal heights **P**/**Q** are 70:30 ± 2. - MS (MAT 90, 40°C); *m/z* (%): 326 (99) [M^+], 293 (12) [M^+- CH_3OH - H; $C_{14}H_{17}N_2O_3S^+$; ^{13}C 1.8/1.8], 267 (8.5) [M^+- CO_2CH_3; ^{13}C 1.22/1.26], 239 (60) [M^+- H_2C=N-CO_2CH_3, $C_{12}H_{17}NO_2S^+$, ^{13}C 8.0/7.6; (^{34}S+$^{13}C_2$) 3.1/2.6], 235 (19) [267 - S; ^{13}C 2.8/3.3; no ^{34}S], 208 (100) [M^+- S-CH=N-CO_2CH_3,

$C_{12}H_{18}NO_2^+$, **7**, ^{13}C 13/12, no ^{34}S], 207 (39), 206 (45) [$C_{12}H_{16}NO_2^+$], 180 (13) [$C_{11}H_{16}S^+$], 166 (63) [$C_{10}H_{14}S^+$, $\mathbf{1}^+$; ($^{34}S+^{13}C_2$) 3.1/2.8], 165 (15), 164 (15), 160 (19) [M^+- 1, $C_5H_8N_2O_4^+$, $H_2C{=}N^+$(E)-NE], 149 (68) [208 - CO_2CH_3, $C_{10}H_{15}N^+$], 133 (21) [166 - SH], 132 (19), 117 (10), 106 (10), 105 (10), 93 (16), 91 (36) [$C_7H_7^+$], 88 (26) [CH_3O_2C-N=NH ?], 79 (32), 77 (14). - Anal. for $C_{15}H_{22}N_2O_4S$ (326.4): calcd C 55.19, H 6.79, N 8.58, S 9.82; found C 55.41, H 7.07, N 8.53, S 9.88.

Table 2. Dynamic ^1H NMR (400 MHz) data for the equilibration of conformations **P** and **Q** of cycloadduct **5** in various solvents (L = low-frequency signal, H = high-frequency signal; for X, see text)

T_C (°C)	Process **P** + **Q**	$\Delta\nu$ (Hz)	k_P (s^{-1})	k_Q (s^{-1})	$\Delta G_P^{\ddagger}$ (kcal mol^{-1})	$\Delta G_Q^{\ddagger}$
a. $CDCl_3$, Isomer ratio **P/Q** = 70:30, X = 2.176						
Ester methyl singlets ($\delta_{H,P}$ 3.745, 3.762; $\delta_{H,Q}$ 3.751, 3.798 at 25°C)						
40	L + L	2.15	1.86	4.35	18.0	17.4
b. Cl_2CD-$CDCl_2$; Isomer ratio **P/Q** = 68:32, X = 2.123						
Ester methyl singlets ($\delta_{H,P}$ 3.646, 3.650; $\delta_{H,Q}$ 3.656, 3.673 at 25°C)						
37	L + H	2.44	2.31	4.91	17.7	17.2
63	H + L	10.4	9.83	20.9	18.2	17.7
AB Spectra of 5'-H_2 ($\delta_{H,P}$ 4.30, 4.81; $\delta_{H,Q}$ 4.35, 4.69 at 25°C)						
68	L + L	19.7	18.6	39.5	18.1	17.6
87	H + H	56.0	53.0	113	18.4	17.8
c. $C_6D_5NO_2$, Isomer ratio **P/Q** = 66:34, X = 2.069						
Ester methyl singlets ($\delta_{H,P}$ 3.76, 3.83; $\delta_{H,Q}$ 3.74, 3.80 at 25°C)						
65	L + L	7.78	8.03	15.6	18.5	18.0
65	H + H	8.22	8.49	16.5	18.4	18.0
AB Spectra of 5'-H_2 ($\delta_{H,P}$ 4.51, 5.05; $\delta_{H,Q}$ 4.58, 4.87 at 25°C)						
82	L + L	28.8	29.7	57.6	18.5	18.0
96	H + H	59.3	61.2	118.9	18.7	18.3

(b) *^{13}C NMR spectrum (100 MHz) in Cl_2CD-$CDCl_2$ at 120°C.* The δ_C are by 0.2 - 0.4 ppm greater than the weighted averages of **P** and **Q** in $CDCl_3$ at 25°C; the assignments are unequivocal. The broadening of some signals shows incomplete "recovery" after coalescence of **P** and **Q** absorptions. δ 26.94, 27.00, 35.70, 37.35 (4 CH), 34.36 br, 35.27, 36.30, 37.79, 38.18 (5 CH_2), 48.79 (C-5'), 53.11, 53.58 (2 OCH_3), 89.80 (C-2), 156.54 (2 C=O).

(c) *Temperature dependence of ^1H NMR spectrum (400 MHz) in $CDCl_3$.* According to measurements at 12 temperatures from -50°C to +50°C, the ν_H (OCH_3) are fairly linear functions of T (K) and allow the extrapolation to $\Delta\nu$ at T_C (Table 2). The AB spectra of **P** and **Q**, due to 5'-H_2, show only small changes of ν from -50°C to +50°C; neither splitting nor coalescence occurs, but the lines broaden at +50°C. The variation of the **P/Q** ratio, determined from the integrals of the AB spectra, is small and within error limits.

The consistency of the 70:30 ratio from the heights of ^{13}C signals is greater.

(d) *^1H NMR spectra in Cl_2CD-$CDCl_2$ from 0°C to 120°C.* The small $\Delta\delta_H$ of the OCH_3 singlets for **P** did not allow the pairing of **P** and **Q** signals with certainty; 1 + 3 and 2 + 4 furnished more consistent results (Table 2) than 1 + 4 and 2 + 3. The shape of the combined signal after the second coalescence remains asymmetric up to 80°C; the separation of the two sharpening peaks begins at 85°C, but the two signals of 3'- and 4'-CO_2CH_3 at 100°C (δ 3.695, 3.701) are still merged at the base and differ in height. Eleven spectra of the AB systems (5'-H_2) from 0°C to 120°C reveal T_C 68°C and 87°C. $\Delta\nu$ of **P**,**Q** pairs at T_C were obtained by graphic extrapolation. The low-frequency A part is at 100°C a doublet with ^2J = 7.6 Hz, whereas the B part appears still as a broad hump. The ratios **P**/**Q** at 0 - 40°C fluctuate from 69:31 to 65:35 in the spectral integrals with 68:32 as an average. Therefore, the temperature dependence of the equilibrium constant (**P**/**Q**) was neglected in the evaluation of k_P and k_Q (Table 2).

(e) *^1H NMR spectra in [D_5]nitrobenzene from 25°C to 149°C.* Here, as in the other solvents, the spectrum after returning from the high temp. to 25°C was identical with the original one. The integrals of the AB spectra (5'-H_2) indicated 66:34 as average for **P**/**Q**. After coalescence, the d with ^2J = 7.5 Hz developed in the A part at 100°C (δ 4.47) and became recognizable in the B part at 137°C (δ 4.90). Before the signals sharpened again, the band broadening at 149°C wiped out the doublet character, due to the beginning of the next dynamic process.

(f) In the bandshape equation for unequal concentrations of equilibrium partners,[7,8] Δp is the difference of the mole fractions of **P** and **Q**, and the function $X = 2\pi\,\delta\nu\,\tau_C$ connects the lifetime τ_C with $\delta\nu$ at T_C. X was taken from a table of selected Δp values.[31]

$$k_P = (1-\Delta p)/2\tau_C \text{ and } k_Q = (1+\Delta p)/2\tau_C$$

are introduced into the Eyring equation for the evalution of $\Delta G_P^{\neq}$ and $\Delta G_Q^{\neq}$.

Spiro[adamantane-2,2'-(1,3,4)-thiadiazolidine]-3',4'-dicarbox-(*N*-phenylimide) (22): *4-Phenyl-1,2,4-triazoline-3,5-dione* (**21**, 2.20 mmol) and 2.00 mmol of **2** in 5 ml of abs. THF were reacted and worked up, as described above. In the quantitative ^1H NMR analysis, the s at δ 4.82 indicated 55% of **22**. The methanolic solution deposited 310 mg (44%), mp 156-158°C. - IR (KBr): ν 693 cm^{-1} w, 759, 768 m (arom. CH out-of-plane deform.), 1402 st; 1494 m, 1595 w (C_6H_5 ring vibr.); 1720 vst, 1768 m (C=O). - ^1H NMR: δ 1.7 - 2.8 (m, 14 H), 4.82 (s, 5'-H_2), 7.2 - 7.5 (m, C_6H_5). Anal. for $C_{19}H_{21}N_3O_2S$ (355.4): calcd C 64.20, H 5.96, N 11.82, S 9.02; found C 64.04, H 6.02, N 11.83, S 9.02.

***Adamantanethione S-Ethylide* (18a)**

2',5'-Dihydro-5'-methylspiro[adamantane-2,2'-(1,3,4)-thiadiazole] (17a): Freshly sublimed adamantanethione (**1**, 498 mg, 3.00 mmol) in 3 ml of diethyl ether at 0°C was treated dropwise with ethereal diazoethane, until the yellow color persisted. After evaporation, **17a** crystallized from pentane at -78°C; 617 mg (93%) of colorless prisms, mp 41-42°C, was obtained (colorless oil).[28] - IR (KBr): $\tilde{\nu}$ 1450 cm^{-1} st (N=N str), 1582 m. - ^1H NMR: δ 1.75 (d, ^3J = 7.0 Hz, CH_3), 1.8 - 2.2 and 2.45 - 2.95 (m, 14 H), 5.87 (q, ^3J = 7.0 Hz, 5'-H). - MS (30°C); *m/z* (%): 222 (< 1) [M^+], 194 (71) [M^+- N_2, **18a**$^+$], 179 (19), 166 (69) [$C_{10}H_{14}S^+$, **1**$^+$], 162 (100) [M^+- N_2 - S; no ^{34}S peak], 147 (10), 133 (14) [**1**$^+$ - SH], 119 (29), 105 (52), 91 (70) [$C_7H_7^+$], 79 (66). - Anal. for $C_{12}H_{18}N_2S$ (222.3): calcd C 64.82, H 8.16, N 12.60, S 14.42; found C 64.78, H 8.19, N 12.51, S 14.65.

Dimethyl 5'-methylspiro[adamantane-2,2'-(1,3,4)-thiadiazolidine]-3',4'-dicarboxylate (19a): **17a** (444 mg, 2.00 mmol) and 322 mg (2.20 mmol) of **4** in 4 ml of absol. THF were stirred at 60°C (oil-bath) for 5 h. After exchange of the THF by $CDCl_3$, the ^1H NMR analysis (δ 5.24 - 5.55, 2 q, due to 5'-H) showed 93% of **19a**. PLC with petroleum ether/acetone (9:1) furnished 487 mg of colorless oil as main fraction which crystallized from pentane: 359 mg (53%), mp 87-89°C. - IR (KBr): $\tilde{\nu}$ 1234 cm^{-1}, 1252, 1284 st (C-O), 1452 st; 1708, 1741 vst (C=O). - ^1H NMR (400 MHz): **P** and **Q** signals ~ 70:30, δ 1.50, 1.48 (2 d, ^3J = 6.1 Hz, 5'-CH_3), 1.60 - 3.20 (m, 14 H), 3.736, 3.75 (2 s, 2 OCH_3 of **P**), 3.738, 3.81 (2 s, 2 OCH_3 of **Q**), 5.44, 5.33 (2 q, ^3J = 6.1 Hz, 5'-H). - ^{13}C NMR (100 MHz, DEPT): **P/Q** = 72:28, determined from heights with higher accuracy than from ^1H integrals; adamantane system, **P** and **Q**, δ 26.60/26.55, 26.62/26.69, 35.30/35.33, 37.14/37.46 (4 CH), 33.80/34.33, 34.97/35.10, 35.92/35.85, 37.50/37.55, 37.69/37.78 (5 CH_2), 89.99/89.77 (C-2); 22.42/22.81 (5'-CH_3), 53.20/53.40, 53.26/53.31 (2 OCH_3), 60.99/61.04 (C-5'), 155.87/154.36, 156.73/156.63 (2 C=O). - MS (MAT 90, 60°C); *m/z* (%): 340 (66) [M^+; ^{13}C 11.7/12.4], 280 (43) [M^+- HCO_2CH_3; ($^{34}S+^{13}C_2$) 2.4/2.2], 249 (22) [M^+- CO_2CH_3 - S; ^{13}C 3.4/3.4, no ^{34}S peak], 239 (69) [M^+- $CH_3CH{=}NCO_2CH_3$, $C_{12}H_{17}NO_2S^+$; ^{13}C 9.2/10.4, ($^{34}S+^{13}C_2$) 3.6/3.7, same peak in MS of **5**], 221 (11), 208 (100) [$C_{12}H_{18}NO_2^+$, **7**; ^{13}C 13.3/13.2, $^{13}C_2$ 0.8/1.2, no ^{34}S], 207 (9), 206 (18), 205 (9) [cascade as observed for **5**], 194 (2.4) [$C_{12}H_{18}S^+$, **18a**$^+$], 180 (6.0) [$C_{11}H_{16}S^+$, **3**$^+$; ($^{34}S+^{13}C_2$) 0.7/0.6], 174 (90) [$C_6H_{10}N_2O_4^+$, M^+- **1**], 166 (72) [$C_{10}H_{14}S^+$, **1**$^+$; ($^{34}S+^{13}C_2$) 3.6/3.0], 149 (13), 133 (9) [**1**$^+$ - SH], 115 (13) [$C_3H_3N_2O_3^+$, CH_3O_2C-N=N-C$\equiv$O$^+$], 103 (26), 91 (17) [$C_7H_7^+$], 79 (16). - Anal. for $C_{16}H_{24}N_2O_4S$ (340.4): calcd C 56.45, H 7.11, N 8.23, S 9.42; found C 56.52, H 7.06, N 8.02, S 9.51.

***Thiobenzophenone S-Methylide* (15b)**

Dimethyl 2,2-Diphenyl-1,3,4-thiadiazolidine-3,4-dicarboxylate (16b): **4** (1.46 g, 10.0 mmol) was added to the solution of 10.0 mmol of **14b**, prepared from 1.98 g of thiobenzophenone and 10 mmol diazomethane in 8 ml of diethyl ether at -78°C.[32] After 6 h at -45°C, the solvent was removed, and the residue treated with diethyl ether/hexane: 2.57 g (72%) of **16b**, mp 98-100°C (dec) after recrystallization from ether. - ^1H NMR: δ 3.28, 3.46 (2 s, 2 OCH_3), 4.63, 5.13 (AB, ^2J = 9.8 Hz, 5-H_2), 6.8 - 7.8 (m, 2 C_6H_5). - MS (90°C); *m/z* (%): 358 (37) [M^+], 270 (17) [$C_{15}H_{12}NO_2S^+$], 239 (19), 212 (13) [$C_{14}H_{12}S^+$, **15b**$^+$], 211 (14), 208 (17), 198 (100) [$C_{13}H_{10}S^+$, ^{13}C 14.5/16.1, ($^{34}S+^{13}C_2$) 5.4/5.7], 180 (20) [$C_{14}H_{12}^+$], 165 (52) [$C_{13}H_8^+$, fluorenyl$^+$], 121 (21) [C_6H_5-C$\equiv$S$^+$], 118 (16), 105 (11) [$C_8H_9^+$], 91 (8) [$C_7H_7^+$], 77 (45) [$C_6H_5^+$], 59 (28) [$CH_3OC{\equiv}O^+$]. - Anal. for $C_{18}H_{18}N_2O_4S$ (358.4): calcd C 60.32, H 5.06, N 7.82; found C 60.63, H 4.92, N 7.88.

2,2-Diphenyl-1,3,4-thiadiazolidine-3,4-dicarboxy-(*N*-phenylimide) (23): Thiadiazoline **14b** (2.99 mmol) and 3.29 mmol of **21** in 13 ml of THF were reacted at -45°C for 8 h; the ^1H NMR analysis (2-methylnaphthalene as standard) indicated 87% of **23**. After removal of the solvent, trituration with diethyl ether afforded 961 mg (83%) of colorless crystals, mp 160-162°C ($CHCl_3$/ether). The $CHCl_3$ solution slowly turned light-blue on storing at daylight. - ^1H NMR: δ 4.80 (s, 5-H_2), 7.3 - 7.5 (m, 15 arom. H). - ^{13}C NMR: δ 48.0 (t, C-5), 85.5 (s, C-2), 125.3, 128.1, 128.9, 129.1 (4 d, 15 arom. CH), 131.5, 137.6 (2 s, 3 arom. C_q), 150.2, 153.2 (2 C=O). - Anal. for $C_{22}H_{17}N_3O_2S$ (387.4): calcd C 68.20, H 4.42, N 10.85, S 8.28; found C 68.05, H 4.23, N 10.81, S 8.22.

Fluorene-9-thione S-Methylide (15c)

Dimethyl Spiro[fluorene-9,2'-(1,3,4)-thiadiazolidine]-3',4'-dicarboxylate (16c): **14c** [33] (2.70 mmol), prepared in 8 ml of THF at -78°C, was treated with 501 mg (3.43 mmol) of **4** in 3 ml of THF at -45°C for 2 h. The ^{1}H NMR analysis (2-methylnaphthalene as weight standard) indicated 88% of **16c** which crystallized from diethyl ether: 793 mg (82%) as colorless prisms, mp 169-171°C. - ^{1}H NMR: δ 3.32, 3.60 (2 s, 2 OCH_3), 4.86, 5.50 (AB, ^2J = 10.6 Hz, 5'-H_2), 7.2 - 7.7 (m, 8 arom. H). - ^{13}C NMR: δ 52.3 (t, C-5'), 52.9, 54.5 (2 q, 2 OCH_3), 80.1 (s, C-2'), 119.9, 120.2, 120.9, 125.1, 2 x 128.2, 129.0, 129.5 (8 d, 8 arom. CH), 138.2, 139.5, 143.5, 148.1 (4 s, 4 arom. C_q), 151.7, 157.8 (2 s, 2 C=O). - Anal. for $C_{18}H_{16}N_2O_4S$ (356.4): calcd C 60.66, H 4.53, N 7.86, S 9.00; found C 60.57, H 4.72, N 7.62, S 8.89.

2,2,4,4-Tetramethyl-3-thioxocyclobutanone S-Methylide (15d)

Dimethyl 2,2,4,4-Tetramethyl-1-oxospiro[cyclobutane-3,2'-(1,3,4)-thiadiazolidine]-3',4'-dicarboxylate (16d): (a) Freshly recrystallized thiadiazoline **14d** [34,35] (396 mg, 2.00 mmol) and 2.20 mmol of **4** in 4 ml of absol. THF were heated at 40°C for 8 h; the half-life for the thermolysis of **14d** is 86 min.[36] The ^{1}H NMR analysis (*sym*-tetrachloroethane as standard) furnished 1.16 mmol (58%) of **16d** (s δ 1.65, CH_3). PLC with CH_2Cl_2/acetone (20:1) afforded 337 mg of a colorless oil; the methanolic solution deposited 303 mg (48%) of **16d** as colorless crystals, mp 110-112°C. - IR (KBr): $\tilde{\nu}$ 1262 cm^{-1}, 1390 st (C-O), 1488 st; 1700, 1757 st (ester C=O), 1785 (ketone C=O). - ^{1}H NMR: δ 1.27 (s, 2 CH_3), 1.41, 1.65 (2 s, 2 CH_3), 3.75 (s, 2 OCH_3), 4.38, 4.58 (AB, ^2J = 7.5 Hz, 5'-H_2). - MS (60°C); *m/z* (%): 316 (2.4) [M^+], 301 (0.8) [M^+- CH_3], 257 (12) [M^+- CO_2CH_3], 246 (100) [$C_9H_{14}N_2O_4S^+$, M^+- dimethylketene], 229 (61) [$C_{10}H_{15}NO_3S^+$, M^+- H_2C=N-CO_2CH_3], 187 (246 - CO_2CH_3), 143 (24), 127 (13), 102 (24). - Anal. for $C_{13}H_{20}N_2O_5S$ (316.4): calcd C 49.35, H 6.37, N 8.86, S 10.14; found C 49.62, H 6.36, N 8.84, S 10.12.

(b) *2,4-Dinitrophenylhydrazone of* **16d**: 120 mg (0.38 mmol) and 1.0 mmol of 2,4-dinitrophenylhydrazine in 3 ml of ethanol and a drop of conc. sulfuric acid were refluxed for 10 h. During 20 h at r.t. 179 mg (95%) crystallized as a mixture (ratio ~ 1:1) of *syn-anti*-isomers, mp 174-178°C (dec) after recrystallization from CH_2Cl_2/pentane. - IR (KBr): $\tilde{\nu}$ 1259 cm^{-1}, 1284, 1312 st (C-O), 1339 vst, 1592 st (NO_2), 1620 vst (C=N), 1710, 1758 st (C=O), 3333 (N-H). - ^{1}H NMR: δ 1.27, 1.46, 1.50, 2 x 1.62, 1.70, 1.77, 1.90 (8 s, 2 x 4 CH_3), 3.80, 3.82 (2 s, 2 OCH_3), 4.38/4.64 and 4.35/4.68 (2 AB, ^2J ~ 8 Hz, 5'-H_2), 7.80 (d, ^3J = 9.5 Hz, arom. 6-H), 8.26 (dd, J = 9.5, 2.8 Hz, arom. 5-H), 8.80 (d, ^4J = 2.8 Hz, arom. 3-H), 11.00 (NH br, disappears with D_2O). - Anal. for $C_{19}H_{24}N_6O_8S$ (496.5): calcd C 45.96, H 4.87, N 16.93, S 6.46; found C 45.92, H 4.92, N 16.87, S 6.47.

2,2,4,4-Tetramethyl-3-thioxocyclobutanone S-Ethylide (18d)

2',5'-Dihydro-2,2,4,4,5'-pentamethylspiro[cyclobutane-3,2'-(1,3,4)-thiadiazole]-1-one (17d): **20** [37] (4.00 mmol) in 3 ml of diethyl ether at 0°C was reacted with ethereal diazoethane, until the yellow color remained for 1 min. The solvent was removed, and **17d** crystallized from 20 ml of pentane at -78°C as colorless leaflets, mp 29-30°C; **17d** is storable for months at -25°C. - IR (film): $\tilde{\nu}$ 1024 cm^{-1}, 1454, 1463 m; 1789 st (C=O). - ^{1}H NMR: δ 1.22 (s, 2 CH_3), 1.25, 1.27 (2 s, 2 CH_3), 1.70 (d, ^3J = 6.8 Hz, 5'-CH_3), 6.02 (q, ^3J = 6.8 Hz, 5'-H). - MS (30°C); *m/z* (%): 212 (1.7) [M^+], 197 (33) [M^+- CH_3], 184 (27) [M^+- N_2], 169 (12) [$C_9H_{13}OS^+$, M^+- N_2 - CH_3], 141 (13), 114 (83) [$C_6H_{10}S^+$, 184 - dimethylke-

tene], 96 (18), 86 (27), 81 (100) [$C_6H_9^+$], 70 (23) [$C_4H_6O^+$], 67 (44) [$C_5H_7^+$]. - Anal. for $C_{10}H_{16}N_2OS$ (212.3): calcd C 56.57, H 7.60, N 13.20, S 15.10; found C 56.53, H 7.53, N 13.23, S 14.83.

Dimethyl 2,2,4,4,5'-Pentamethyl-1-oxospiro[cyclobutane-3,2'-(1,3,4)-thiadiazolidine]-3',4'-dicarboxylate (19d): **17d** (424 mg, 2.00 mmol) and 2.2 mmol of **7** in 4 ml of THF were reacted for 6 h at 45°C. The quantitat. ^1H NMR analysis indicated 63% of **19d** (q δ 5.22). PLC with CH_2Cl_2/acetone (20:1) produced 312 mg (47%), mp 117-119°C (methanol). - IR (KBr): ν 1266 cm^{-1}, 1387, 1448, 1456 st; 1703, 1752 st (ester C=O), 1788 st (ketone C=O). - ^1H NMR: δ 1.28 (s, 2 CH_3), 1.40, 1.62 (2 s, 2 CH_3), 1.52 (d, ^3J = 6.2 Hz, 5'-CH_3), 3.77 (s, 2 OCH_3), 5.22 (q, ^3J = 6.2 Hz), 5'-H). - MS (55°C); *m/z* (%): 330 (2) [M^+], 315 (2.4) [M^+- CH_3], 271 (11) [M^+- CO_2CH_3], 260 (78) [$C_{10}H_{16}N_2O_4S^+$, M^+ - dimethylketene], 229 (100) [$C_{10}H_{15}NO_3S^+$, M^+- $CH_3CH{=}N\text{-}CO_2CH_3$, same fragment from **16d**], 201 (85), 159 (28), 156 (31), 127 (35), 116 (19), 86 (24), 84 (30), 59 (70) [$CH_3OC{\equiv}O^+$]. - Anal. for $C_{14}H_{22}N_2O_5S$ (330.4): calcd C 50.89, H 6.71, N 8.48, S 9.71; found C 51.11, H 6.82, N 8.57, S 9.92.

Acknowledgments

We express our thanks to the *Fonds der Chemischen Industrie*, Frankfurt, for supporting our research work. The *Alexander von Humboldt Foundation* provided X. L. and G. M. with stipends and deserves our thanks. We are indebted to *Reinhard Seidl* for the MS and thank *Helmut Schulz* and *Magdalena Schwarz* for the elemental analyses.

REFERENCES

Dedicated to Professor *Mieczyslaw Makosza*, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, on the occasion of his sixty-fifth birthday.

1. 1,3-Dipolar Cycloadditions, 114; part 113 see ref. 5.
2. Present addresses: Dr. X. Li, Avery Research Center, Pasadena, CA 91107, USA; Prof. G. Mloston, Institute of Organic and Applied Chemistry, University of Lodz, PL - 90-136 Lodz, Poland.
3. Huisgen, R.; Mloston, G., *Polish J. Chem.* **1999**, *73*, 635-644.
4. Mloston, G.; Huisgen, R.; Huber, H.; Stephenson, D. S., *J.Heterocycl. Chem.*, in press.
5. Mloston, G.; Huisgen, R.; Polborn, K., *Tetrahedron*, in press.
6. Cookson, R. C.; Crab, T. A.; Frankel, J. J.; Hudec, J., *Tetrahedron Suppl.* **1966**, *7*, 355-390.
7. Lynden-Bell, R. M., in *Progress in NMR Spectroscopy*; Emsley, J. W.; Feeney, J.; Sutcliffe, L. H., Eds.; Pergamon Press: Oxford, 1967; Chapter 4.
8. Shanan-Atidi, H.; Bar-Eli, K. H., *J. Phys. Chem.* **1970**, *74*, 961-963.
9. Oki, M.; Iwamura, H.; Hayakawa, N., *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1865-1870. Kurland, R. J.; Rubin, M. B.; Wise, W. B., *J. Chem. Phys.* **1964**, *40*, 2426-2427.
10. Kohata, K.; Fukuyama, T.; Kuchitsu, K., *J. Phys. Chem.* **1982**, *86*, 603-606.
11. Vitkovskaya, N. M.; Dolgunicheva, O. Y.; Frolov, Y. L.; Keiko, U. V.; Voronkov, M. G., *Dokl. Akad. Nauk SSSR* **1977**, *235*, 843-845; Engl. Transl., 749-751.
12. Excellent reviews: (a) Shvo, Y., Conformational Analysis of Hydrazines. In *The Chemistry of Hydrazo, Azo, and Azoxy Groups;* Patai, S., Ed.; John Wiley: New York, 1975; pp 1017-1095. (b) Nelsen, S. F., Hydrazine Stereodynamics. In *Acyclic Organonitrogen Stereodynamics*; Lambert, J. B.; Takeuchi, Y. Eds.; VCH: Weinheim, 1986; pp 89-121.

13. Ottersen, T., *Acta Chem. Scand.* **1974**, *A28*, 1145-1149.
14. Jeffrey, G. A.; Ruble, J. R.; McMullan, R. K.; De Frees, D. J.; Pople, J. A., *Acta Cryst.* **1982**, *38B*, 1508-1513.
15. Ottersen, T., *Acta Chem. Scand.* **1978**, *A32*, 127-131.
16. Dewar, M. J. S.; Jennings, W. B., *J. Am. Chem. Soc.* **1973**, *95*, 1562-1569.
17. (a) Bishop, G. J.; Price, B. J.; Sutherland, I. O., *J. Chem. Soc., Chem. Commun.* **1967**, 672-674. (b) Fletcher, J. R.; Sutherland, I. O., *J. Chem. Soc., Chem. Commun.* **1969**, 706-708.
18. (a) Breliere, J. C.; Lehn, J. M., *J. Chem. Soc., Chem. Commun.* **1965**, 426-427. (b) Anderson, J. E.; Lehn, J. M., *Tetrahedron* **1968**, *24*, 123-135. (c) *id., Tetrahedron* **1968**, *24*, 137-149. (d) Wagner, J.; Wojnarowski, W.; Anderson, J. E.; Lehn, J. M., *Tetrahedron* **1969**, *25*, 657-676. (e) Lehn, J. M.; Wagner, J., *Tetrahedron* **1969**, *25*, 677-689.
19. (a) Price, B. J.; Smallman, R. V.; Sutherland, I. O., *J. Chem. Soc., Chem. Commun.* **1966**, 319-320. (b) Price, B. J., Sutherland, I. O.; Williamson, G. Q., *Tetrahedron* **1966**, *22*, 3477-3490.
20. Offereins, B.; Altona, C.; Romers, C., *Acta Cryst.* **1973**, *B29*, 2098-2103.
21. Electron diffraction: Dallinga, G.; Toneman, L. H., *Rec. Trav. Chim. Pays-Bas* **1968**, *87*, 785-804. Yokozeki, A.; Kuchitsu, K., *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2356-2363.
22. Force field: Altona, C.; Sundaralingam, M., *J. Am. Chem. Soc.* **1970**, *92*, 1995-1999.
23. X-ray of anti-7-norbornenyl 4-bromobenzoate: Macdonald, A. C.; Trotter, J., *Acta Cryst.* **1965**, *19*, 456-463.
24. The authors are highly indebted to Professor *Hendrik Zipse*, Munich, for the AM1 calculation.
25. Nelsen, S. F.; Blackstock, S. C.; Petillo, P. A.; Agmon, I.; Kaftory, M., *J. Am. Chem. Soc.* **1987**, *109*, 5724-5731.
26. Pitzer, K. S.; Donath, W. E., *J. Am. Chem. Soc.* **1959**, *81*, 3213-3218.
27. Krapcho, A. P.; Silvon, M. P.; Goldberg, I.; Jahngen, E. G. E., *J. Org. Chem.* **1974**, *39*, 860-861.
28. Katada, T.; Eguchi, S.; Sasaki, T., *J. Chem. Soc., Perkin Trans. 1* **1984**, 2641-2647.
29. Fisera, L.; Huisgen, R.; Kalwinsch, I.; Langhals, E.; Li, X.; Mloston, G.; Polborn, K.; Rapp, J.; Sicking, W.; Sustmann, R., *Pure & Appl. Chem.* **1996**, *68*, 789-798.
30. (a) Kaftory, M.; Agmon, I., *J. Am. Chem. Soc.* **1984**, *106*, 7785-7793. (b) Agmon, I.; Kaftory, M.; Nelsen, S. F.; Blackstock, S. C., *J. Am. Chem. Soc.* **1986**, *108*, 4477-4484. (c) Nelsen, S. F.; Petillo, P. A.; Chang, H.; Frigo, T. B.; Dougherty, D. A.; Kaftory, M., *J. Org. Chem.* **1991**, *56*, 613-616.
31. Egan, W.; Mislow, K., Princeton University, 1971. The table of X as a function of Δp was published by Sandstrom, J., in *Dynamic NMR Spectroscopy*, Academic Press: London-New York, 1982; pp 81-82.
32. Kalvinsch, I.; Li, X.; Gottstein, J.; Huisgen R., *J. Am. Chem. Soc.* **1981**, *70*, 7032-7033.
33. Huisgen, R.; Kalvinsch, I.; Li, X.; Mloston, G., *Eur. J. Org. Chem.*, submitted.
34. Diebert, C. D., *J. Org. Chem.* **1970**, *35*, 1501-1505.
35. Huisgen, R.; Penelle, J.; Mloston, G.; Buyle Padias, A.; Hall, H.K., *J. Am. Chem. Soc.* **1992**, *114*, 266-274.
36. Measurements by E. Langhals, University of Munich, 1985.
37. Elam, U. E.; Davis, H. E., *J. Org. Chem.* **1967**, *32*, 1562-1565.