Tetrahedron Vol 32, pp 1641 to 1648. Pergamon Press 1976. Printed in Great Britain

THIOCARBONYL YLIDES[1]

REACTIONS AND STEREOCHEMICAL PROPERTIES OF SOME 4-t-BUTYLCYCLOHEXYL DERIVATIVES

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(*Received UK* 31 *December* 1975; *Accepted for publication* 17 *March* 1976)

Abstract—The azine from 4-t-butylcyclohexanone on treatment with hydrogen sulfide under pressure is converted to a mixture of stereoisomeric 1,3,4-thiadiazolidines. Dehydrogenation of this mixture with an alkyl azodicarboxylate afforded in quantitative yield (based on azine) a mixture of the three possible Δ^3-1,3,4-thiadiazolines. These three isomers have been isolated and their structures have been established as *trans,trans*-3,11-di-[1,1-dimethylethyl]-14,15-diaza-7-thiadispiro[5.1.5.2]pentadeca-14-ene(**5**); the *cis,cis*-isomer (**6**), and the *cis,trans*-isomer (**7**). Pyrolysis of either **5** or **6** leads in quantitative yield to *cis,trans*-3,10-di-[1,1-dimethylethyl]thiadispiro[5.0.5.2]tridecane (**8**), the formation of which is rationalized by conrotatory ring closure of the same thiocarbonyl ylide (**24**) formed from either **5** or **6**. Pyrolysis of **7** leads exclusively to a thiirane isomeric with **10** and which is assigned the *cis,cis*-structure (**9**). The thiiranes **8** and **9** are desulfurized by tri-n-butylphosphine to the *anti*- and *syn*-1-(1,1-dimethylethyl)-4-[4-(1,1-dimethylethyl)cyclohexylidene]cyclohexanes (**11** and **12**), respectively. The cycloadditions of the thiocarbonyl ylides derived from **5**–**7** with dimethyl acetylenedicarboxylate and dimethylazodicarboxylate have been examined but stereochemistries have not been assigned to these products. *Cis* additions to the olefins (**11** and **12**) have been investigated with the most attention having been paid to the reactions with osmium tetroxide. The configurations of the glycols expected from these reactions have been correlated by comparison with the three possible glycols (**16**–**18**) obtained from pinacol reduction of 4-t-butylcyclohexanone. These three glycols have been separated and their configurations assigned from PMR and IR data. A discussion of the stereochemical implications of the various results is given.

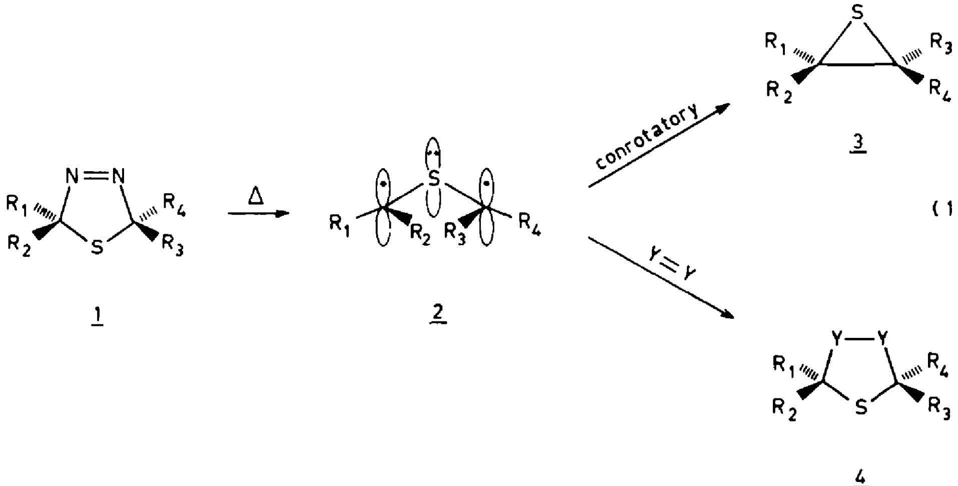
INTRODUCTION

Interest in thiocarbonyl ylides is growing.[3,4] A felicitous route to these reactive intermediates (**2**) is through thermally induced loss of nitrogen from Δ^3-1,3,4-thiadiazolines (**1**).[4] Spontaneous conrotatory ring-closure to a thiirane (**3**) is the common fate of **2** unless an electron deficient dipolarophile is present allowing trapping with retention of configuration as cycloadduct (**4**).

We report here the results of an investigation of thiocarbonyl ylides in which are incorporated cyclohexyl rings deprived of conformational mobility by substitution in the 4-position with a t-Bu group.[5]

RESULTS

A. *Preparation of the thiocarbonyl ylide precursors and assignment of stereochemistry.* The isomers **5**–**7** were prepared by the reaction sequence of eqn (2). Addition under pressure of hydrogen sulfide[3b,6] to the azine of 4-t-butylcyclohexanone followed by dehydrogenation with an alkylazodicarboxylate[7] afforded in virtually quantitative yield a mixture of **5**–**7** (R = t-Bu). The symmetrical isomers **5** and **6** were readily separated from **7** by dissolution in n-pentane in which the latter is totally insoluble; **7** is, however, sparingly soluble in carbon tetrachloride.† Chromatography over aluminum oxide allowed separation of **5** from **6**.



(1)

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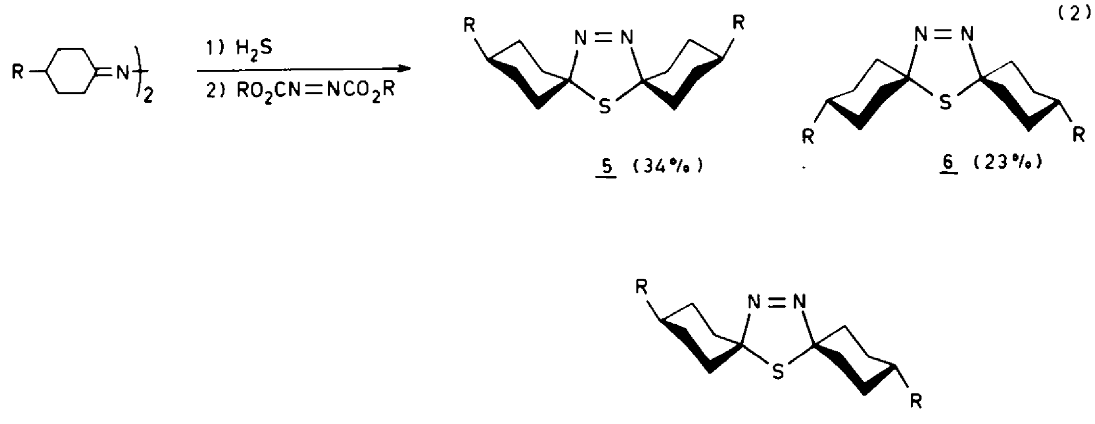
†In previous work[4a] **6** was isolated and identified and its reactions were briefly studied. Isomers **5** and **7** were found on more thorough investigation of these reaction conditions. Note that in eqn (16) of Ref. 4a that structures **52** and **53** are (unintentionally) drawn ambiguously. The experimental results here supercede the data given in Ref. 4*a* for **6** and its reaction products.



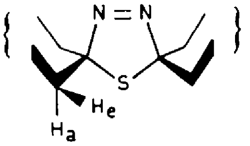
(2)

5 (34%)

6 (23%)

7 (43%)

In its PMR spectrum **7** shows nonequivalent t-Bu groups thereby uniquely defining its stereochemistry. The inequivalence of the two rings is nicely substantiated by the CMR spectrum (Table 1). That **5** and **6** have symmetrical structures is indicated by the PMR spectra (single t-Bu absorption) and the CMR spectra.‡ Distinction between the two stereoisomers is based on the results of experiments with Eu(FOD)$_3$ shift reagent, which is expected to complex most strongly with the azo portion of the molecule.[8] In CDCl$_3$ solution with one of the symmetrical isomers on addition of Eu(FOD)$_3$ two sets of absorptions shift downfield (observed on 100 MHz instrument). Most strongly shifted (2.79 ppm/eqv. Eu(FOD)$_3$) is a broad absorption having the appearance of a triplet, J = *ca.* 13 Hz, with a total base width of 35 Hz. Each peak of the "triplet" is further split into a doublet, J = *ca.* 3 Hz. The second absorption, essentially a doublet, J = *ca.* 13 Hz, is shifted 1.7 ppm/eqv. Eu(FOD)$_3$ downfield. Each set of absorptions integrated for four protons. Plots of Δ chemical shift against Eu(FOD)$_3$ were linear up to a 1 : 1 ratio (upper limit investigated). Saturation of the lower field triplet causes collapse of the doublet absorption to a broad singlet with no other pronounced changes in the spectrum. The other symmetrical isomer with Eu(FOD)$_3$ exhibits no systematic changes. Examination of models **5** and **6** (partial structures shown) shows that in **6** the protons H$_a$ project into the vicinity of the azo functionality whereas this is not true for **5**. The symmetrical isomer showing shift phenomena with Eu(FOD)$_3$ is therefore **6**; the triplet and doublet absorptions that are shifted are assigned respectively to H$_a$ and H$_e$.[9]



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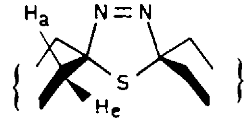

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Table 1. Proton decoupled CMR spectra (25.2 MHz) of various 4-t-butylcyclohexyl derivatives

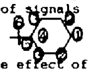
Chemical Shifts Downfield Relative to TMS^{a,b}

Compound	C(1)^{e}		CH$_2$(2)^{c,d}		CH$_2$(3)^{c,d}		CH(4)^{c}		C(5)^{c}		CH$_3$(6)^{b}		other (7)
5	106.5		42.4		25.6		47.2		32.4		27.5		
6		110.7		39.5		25.2		46.7		32.3		27.5	
7	107.0	110.5	42.5	39.3	25.7	25.2	47.1	46.5	32.4	32.3	27.5		
8	57.6	60.9	35.8	34.4	28.1	26.6	47.0	47.6	32.3	32.4	27.6		
9		60.5		33.8		26.6		47.6		32.4	27.6		
11	128.5		29.7		28.9		48.6		32.4		27.7		
12	128.6		29.7		28.8		48.6		32.3		27.6		
13		58.7		34.1		26.9		47.4		32.5	28.0		CH$_2$:53.8
14	57.2		33.5		25.0		47.4		32.7		27.9		CH$_2$:52.9
19 or 20		80.1		37.2^{e}		27.2^{e}		46.7		32.2	27.5		CH$_3$O:52.8
				38.4		24.9							
21	76.5	81.9	37.7^{e}	42.3^{e}	25.7^{e}	27.6^{e}	46.2	47.0	32.3	32.2	27.5		CH$_3$O:53.1
			32.7	37.7	25.2	25.9							53.7

[a] Chemical shifts measured in CDCl$_3$ at ambient temperature

[b] All signals assigned from multiplicity of signals in proton coupled spectra

[c] Numbering in table according to scheme



[d] Assigned on the basis of common distance effect of electronegative substituents: G.C. Levy and G.L. Nelson, "^{13}C N.M.R. For Organic Chemists", Wiley Interscience, New York, N.Y. (1972).

[e] The methoxycarbonyl groups on nitrogen must be trans-arranged with a rate of pyramidal inversion of nitrogen slow with respect to the cmr time scale; the plane present in other molecules examined here is lost leading to multiplicity of signals.

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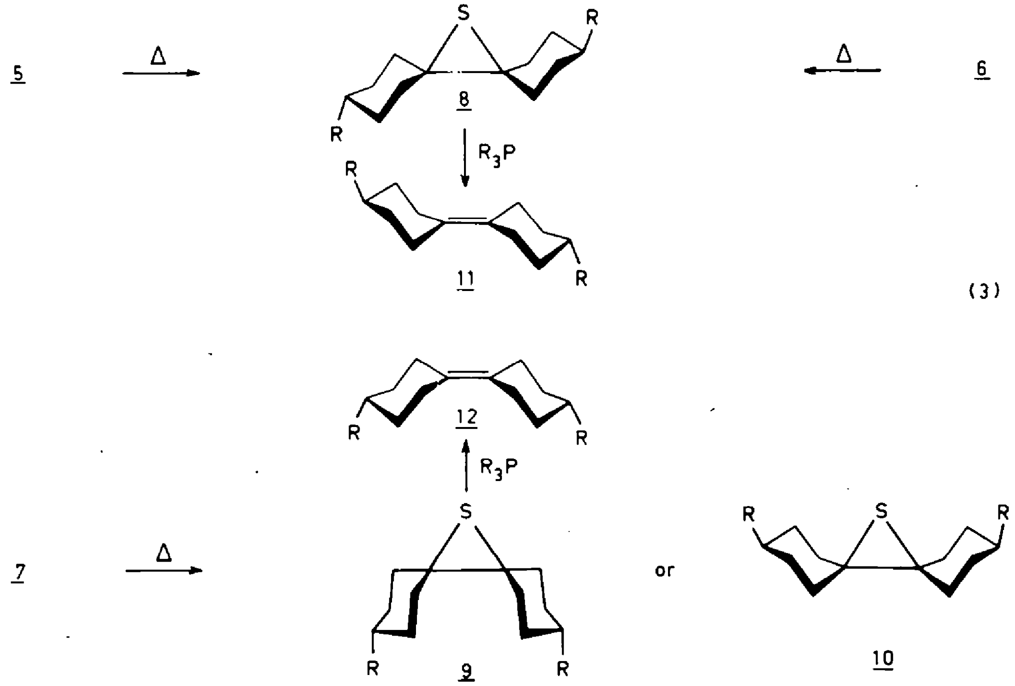
‡With the use of the adjective "symmetrical" in regard to spectra we mean that there is a symmetry element present (C_2 or σ) that causes in the opposing cyclohexyl rings the atoms or groups under discussion to be equivalent with regard to NMR observation. This qualification is necessary since most of the compounds mentioned in this article are "symmetrical" in the sense that they have at a minimum a plane of symmetry in the length of the molecule perpendicular to the cyclohexyl rings.

In accord with these assignments **7**, to which configuration had been assigned by other criteria, with Eu(FOD)$_3$ in CDCl$_3$ solution exhibited modest downfield shifts of a broad triplet, J = *ca.* 13 Hz, 1.0 ppm/eqv Eu(FOD)$_3$ and a broad doublet, J = *ca.* 13 Hz, 0.1 ppm/eqv Eu(FOD)$_3$. The integration for each absorption was for *two protons.* This is obviously in complete agreement with the argumentation advanced above.

B. *Pyrolysis of the isomeric thiocarbonyl ylide precursors and structural assignments of the products.* Pyrolysis in boiling methylcyclohexane of either **5** or **6** separately or as a mixture (most convenient for preparative purposes) gave the same thiirane (**8**) in quantitative yield. All the spectroscopic and chromatographic techniques employed gave no evidence for detectable amounts of other isomers. Pyrolysis of **7** under the same conditions gave a *single* thiirane nonidentical with **8**; structures **9** or **10** are possible (but not a mixture of the two). With tri-n-butylphosphine in boiling xylene the thiiranes were converted in excellent yield to the isomeric olefins **11** and **12**. These conversions are shown in eqn (3) (R = t-Bu).



(3)

Assignment of structure to **8** is based on the observation of two t-Bu groups in the PMR spectrum and this conclusion is firmly supported by the CMR data (Table 1). The PMR and CMR data for the product from **7** establish the reflection symmetry of the rings but provide no basis for a distinction between **9** and **10**. We hoped that the CMR absorptions observed for the nonequivalent spiro C atoms of **8** at 57.6 and 60.9 ppm from TMS could be assigned. If this were possible, the close correlation of the position of the spiro carbon absorption in symmetrical **9/10** (60.5 ppm downfield from TMS) with the most downfield spiro carbon absorption in **8** would give a basis for distinction between **9** and **10**. To provide models that might aid in assignment to the spiro C atoms, **13**[10] and **14**[11] were prepared and their spectra were examined. The observation that the spiro C atom in **13** (oxygen equatorial) is shifted slightly downfield relative to **14**

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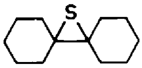

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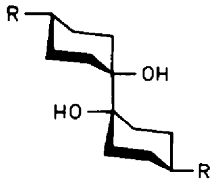
(58.7 ppm compared to 57.2 ppm, Table 1) suggests, but certainly does not demand, assignment of structure **9** to the symmetrical thiirane.

Compelling evidence for the correctness of structure **9** is provided, however, by the relative rates of desulfurization of **8** as compared with **9/10**. Tri-n-butylphosphine was used for preparative conversions to olefins **11** and **12** and it was observed that in boiling xylene **8** desulfurized much more slowly than the symmetrical **9/10**. This difference in rate is even more pronounced with triphenyl phosphine: the symmetrical thiirane from **7** is fully desulfurized within 2 hr in boiling xylene whereas **8** is *ca.* 10% desulfurized after 24 hr in boiling xylene. The relative rates for desulfurization compared to *non*-t-Bu substituted model **15** in boiling xylene with triphenylphosphine are approximately in the order **8**:**9/10**:**5** is 1.0:120:1500. The slow rate of desulfurization of **8** with respect to **9/10** is explainable as a classical case of rate differences in attack at equatorially as compared to axially located substituents.[12] Reaction rates for oxidation at sulfur located axially on a rigid cyclohexane are lower than in the equatorial isomer because of increased steric requirements in the transition state leading to 1,3-diaxial interactions.[13] Desulfurization of thiiranes with phosphines is known by mechanistic criteria[14] to involve attack at sulfur followed by concerted loss of olefin. Increased steric repulsions in the transition state are to be expected. Thiirane **8** has 2 sets of 1,3-interactions, **10** would have 4 sets of interactions and **9** none. The available data indicate the necessity of assigning structure **9** rather than **10**. Inspection of models reveals that **9** is considerably more hindered than **10** owing to van der Waals interference of axial hydrogens between the two rings.

C. *Structural verification and stereochemistry of hydroxylation of olefins* **11** *and* **12**. The desulfurization of thiiranes with phosphines or phosphites proceeds with retention of configuration on the alkene, at least in all cases known to us.[15] On this basis there is no reason for entertaining doubts about the structural assignments for **11** and **12**. However, the close structural similarity of these two isomers (in the anticipated chair conformations they belong, respectively, to the point groups C_{2v} and C_{2h}) leads to virtually superimposable PMR, CMR and IR spectra. The melting points do differ, 183–183.5° for **11** and 137–138° for **12**, thereby providing reassurance from classical chemistry that one indeed has two different compounds in hand. In view of the rather subtle difference between **11** and **12** an unambiguous demonstration of structure was deemed mandatory. A *cis*-addition reaction of a symmetrical reagent would provide an excellent opportunity to establish configuration since such an addition would destroy the C_{2h} symmetry of **11** whereas C_{2v} symmetry would be maintained in **12** but the possibility of structural isomerism of products is opened by the availability of stereochemically nonequivalent equatorial and axial faces of **12**.[16] To this end *cis*-hydroxylation has been studied.

To provide the necessary models 4-t-butylcyclohexanone was subjected to pinacol reduction with aluminum amalgam.[17] On fractional crystallization from methanol first **16** precipitated and was followed by **17**; chromatography of the mother liquors gave **18**.



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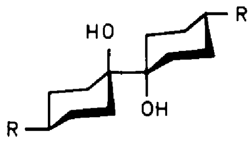

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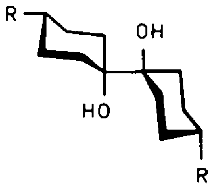

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Structural assignment to **18** is based on the observation of two t-Bu absorptions of equal intensity in the PMR spectrum in C_6D_6. Identification of the symmetrical isomers **16** and **17** is accomplished on the basis that for one isomer, in addition to the broad, featureless, hydrogen bonded hydroxyl IR absorption at 3500 cm^{-1} common to all three isomers, there was a sharp nonhydrogen bonded absorption at 3610 cm^{-1}. The latter absorption increased in relative intensity with decreasing concentration of glycol. Examination of models shows clearly that **16** cannot assume without severe steric interactions between axial protons in the opposing rings the eclipsed conformation required for *intra*molecular H-bonding. The isomer showing concentration dependent nonhydrogen bonded hydroxyl absorption is therefore **16**.

Treatment with osmium tetroxide[18] of **11** afforded in high yield exclusively **18** confirming the correctness of structure **11**. With **12** a mixture of **16** and **17** in a ratio of 7:3 was obtained again in excellent yield. Attack on the less hindered equatorial face of **12** is favored only to a small extent. Note that there are no 1,3-diaxial interactions on this face (but four 1,2-interactions from the axially oriented allylic protons[19] and that the axial face of **12** is somewhat enclosed owing to the overall concavity of the molecule on this side. Further aspects of the chemistry of **11** and **12** will be reported on subsequently.

D. *Cycloaddition reactions with* Δ^3*-1,3,4-thiadiazolines,* **5–7**. Intermediates derived from **5–7** could be trapped readily by cycloaddition with dimethyl azodicarboxylate or, less well, with dimethyl acetylenedicarboxylate. With the former dipolarophile both **5** and **6** gave the same product in 95% yield (10-fold dipolarophile excess). This was, as well as could be determined by the spectroscopic observations tabulated in Table 1 and described further in the Experimental, a stereochemically homogeneous material having structure **19a** or **20a** (R = t-Bu, eqn 4). Oxidation to the sulfoxide **19b** or **20b** was carried out in the hope of using shielding phenomena to determine configuration.[20] Results were inconclusive, however. At this time there appear to be no solid experimental observations on which to base a distinction between **19** and **20**.

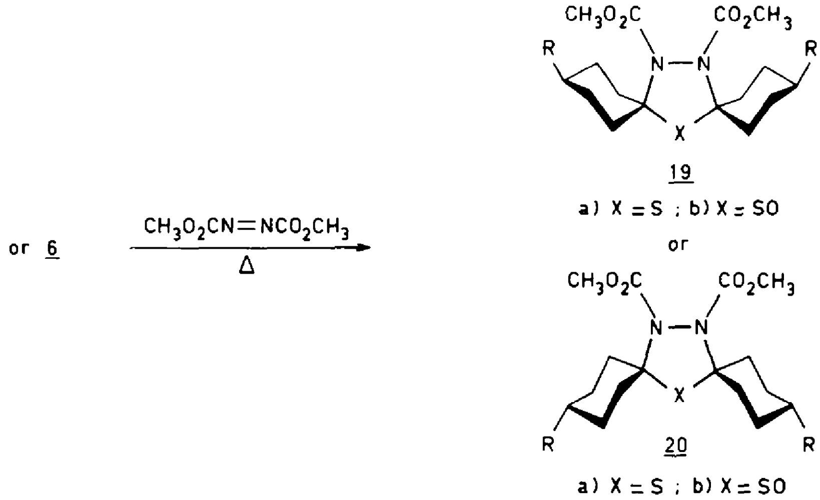
With **7** as expected a single cycloaddition product was formed to which structure **21** (R = t-Bu, eqn 5) can be assigned without hesitation owing to the spectroscopically observed (Table 1) nonequivalence of the cyclohexyl rings.

Additions of **5** and **6** with dimethyl acetylenedicarboxylate proceeded sluggishly. The properties of the cycloadducts are described in the Experimental. With **7** no detectable amount of trapping occurred.

DISCUSSION

In previous work[4a] we established on the basis of kinetic analysis and trapping experiments that **22** on pyrolysis yields the thiocarbonyl ylide **23** (eqn 6), the lifetime of which is too short to permit direct experimental observation. Nothing could be said about conformational effects in **23** or its precursor **22**. An avenue of attack on that problem is opened by resort to the classical method of attaching t-Bu groups at the 4-position of the cyclohexyl rings to restrict conformational mobility and to introduce the potential for stereoisomerism.

The obtainment of identical ring-closure (**8**) and cycloaddition (**19** or **20**) products from the symmetrical thiadiazolines **5** and **6** provides justification for the presumption that a common thiocarbonyl ylide **24**, R = t-Bu, is formed. In view of the differing configuration of the spiro atoms in **5** and **6** it follows that these carbons in **24** must be effectively planar (rapidly interconverting sp^3 configurations are kinetically indistinguishable from a planar model). In idealized geometry **24** has a symmetry plane bisecting the C–S–C bond angle. Inspection of models indicates that buttressing of the equatorial protons



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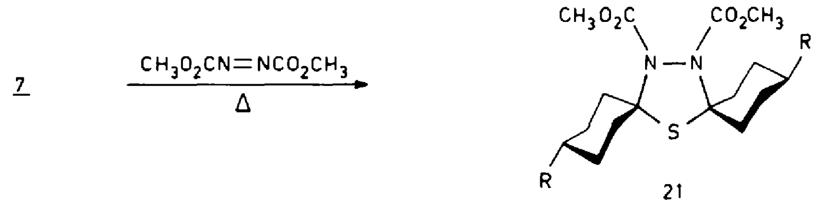

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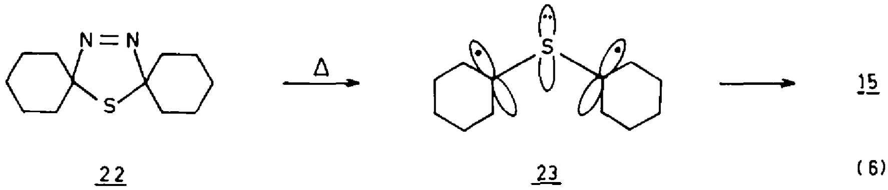

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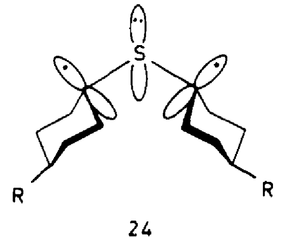

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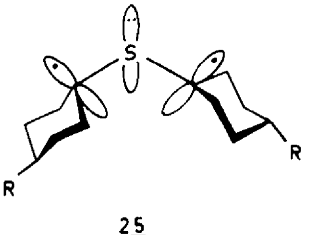

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H_c is likely in this conformation. Mild tilting of the rings, one up and one down or both up (down) relieves this difficulty. In common with other thiocarbonyl ylides **24** undergoes *conrotatory* ring closure. The electronic reasons for conrotatory rather than disrotatory ring-closure are well understood.[21] The two possible directions for conrotatory ring-closure are seen to be enantiomeric.

Loss of nitrogen from **7** gives thiocarbonyl ylide **25**, in which there is a C_2 axis that bisects the C–S–C bond angle. As in **24** a fully planar thiocarbonyl ylide segment is unlikely owing to severe buttressing of the hydrogens H_c. The interested reader who inspects a model of **25** will see that this interaction is most effectively relieved by tilting the two cyclohexyl rings in a manner commensurate with the experimentally observed axial-axial conrotatory ring-closure. Other possible tilting motions—for example, in a direction consistent with equatorial-equatorial ring-closure—are less effective owing to development of potential H_c–H_a interactions. The postulation of relief of buttressing interactions provides perhaps one reason for exclusive axial-axial ring-closure. Other potential causes can also be found although we must emphasize that the exercise of isolating effects, although instructive, is artificial in that it is the simultaneous operation of a host of factors, many subtle, the lead to the observed result.

We recognize first that a remarkably common attribute of exothermic carbon-carbon bond reactions is that in cases where structural isomerism is possible, the more strained isomer predominates.[22] There is no general theory to explain this puzzling observation although a suggestion based essentially on hyperconjugative effects ("steric attraction") to rationalize some special cases has been offered by Hoffmann *et al.*[23] The present example does seem less surprising considered against this background although the absolute discrimination observed in favor of one isomer is unexpected.

For the sake of simplicity (and argument) one may adopt the exaggerated standpoint that the ring-closure at hand may be viewed as an extremely exothermic addition of a carbanion to a carbonium ion forced to follow a conrotatory pathway for reasons of conservation of orbital symmetry. For the addition of carbanions to ketones in cases where the transition state is presumably reached early, there is a distinct preference for axial addition despite potential 1,3-diaxial interactions, which presumably develop late.[24] Equatorial addition is presumably less advantageous owing to the unavoidable torsional effect associated with conversion of sp^2 carbon to sp^3 hybridization. This effect is avoided in axial addition. Such an argument extrapolates well to the case of **25** and provides an acceptable rationale for the occurrence of exclusive axial–axial bond formation in the likely quite exothermic ring-closure. Further speculation in absence of information concerning the actual geometry of **25** is unwarranted.

EXPERIMENTAL

All m.ps were determined with a calibrated m.p. block or with a Mettler automatic m.p. apparatus. UV, IR, NMR spectra, and mass spectra were obtained using common laboratory instruments.

Chemicals cited without reference were either in stock or were prepared following well-described procedures. Elemental analyses were carried out in the analytical laboratory of this university.

Synthesis and isolation of trans,trans - (**5**), cis,cis - (**6**), *and* cis,trans - 3,11 - di - [1,1 - *dimethylethyl*] - 14,15 - *diaza*-7-*thiadispiro*[5.1.5.2]*pentadeca* - 14 - *ene*(**7**) was carried out as follows. The azine of 4-t-butylcyclohexanone (29.2 g, 96 mmole), m.p. 174–177° was dissolved in *ca.* 150 ml dry CHCl$_3$, a few mg of *p*-toluenesulfonic acid was added and was put in a Parr apparatus converted for use with H$_2$S. A pressure of 1.5–2.5 atm H$_2$S was maintained for 29 hr while the mixture was mechanically shaken. A white ppt had formed after this time. The H$_2$S pressure was relieved, sufficient CH$_2$Cl$_2$ was added to dissolve the solid material, and diethyl azodicarboxylate (25 g, 144 mmole, excess) was added with stirring at room temp.; the soln was heated with stirring to 40° for 1.5 hr. The solvent was removed and the solid remaining was extracted with pentane. A portion of the solid dissolved. The insoluble material was collected by vacuum filtration. The pentane soln was washed with NaHSO$_3$ aq until colorless and thereafter once with cold water. After drying over MgSO$_4$ and removal of the solvent there was obtained a white solid which was chromatographed over 100 g silica gel using 98% benzene/2% ether. There was obtained 18.44 g (54.9 mmole, 53%) of a mixture consisting exclusively of **5** and **6** in 60:40 ratio. Preparative layer chromatography on glass plates using silica gel and hexane/benzene (3:2) as eluting middle allowed ready separation. Recrystallization from MeOH gave samples of analytical purity: **5**, PMR (CDCl$_3$) δ0.92 (s, 18, (CH$_3$)$_3$C−) δ1.7–2.15 (complex, 18, ring *H*), IR (KBr) 1580 cm^{-1} (−N=N−); **6**, PMR (CDCl$_3$) δ0.89 (s, 18, (CH$_3$)$_3$C−), δ0.7–2.5 (complex, 18, ring *H*); IR (KBr) 1575 cm^{-1} (−N=N−). Found: C, 71.31; H, 10.72; N, 8.38; S, 9.38. Calc. for C$_{20}$H$_{36}$N$_2$S (**5**): C, 71.37; H, 10.79; N, 8.32; S, 9.52%; Found: C, 71.42; H, 10.73; N, 8.30; S, 9.50. Calc. for C$_{20}$H$_{36}$N$_2$S (**6**): C, 71.37; H, 10.79; N, 8.32; S, 9.52%).

The material that was insoluble in pentane was extracted 6× with 100 ml portions of CCl$_4$ with very vigorous shaking. Combination of the CCl$_4$ extracts followed by removal of the solvent gave 13.74 g (40.9 mmole, 43%) essentially pure **7**, which was recrystallized with some difficulty from a mixture of C$_6$H$_6$, Me$_3$OH, and CH$_2$Cl$_2$; **7** has PMR (CDCl$_3$) δ0.91 (s, 9, $(C\underline{H}_3)_3C$−), δ0.87 (s, 9, $(C\underline{H}_3)_3C$−), and δ1.0–2.5 (complex, 18, ring $\underline{H}$), IR(KBr) 1580 cm^{-1} (−N=N−). (Found: C, 71.31; H, 10.72; N, 8.38; S, 9.38. Calc. for C$_{20}$H$_{36}$N$_2$S (**7**): C, 71.37; H, 10.79; N, 8.32; S, 9.52%).

Further details of the PMR spectra of **5**–**7** are described in the text and the CMR spectra are given in Table 1. All three isomers decomposed at temps depending on the rate of heating when attempts to determine m.ps were made.

Pyrolysis of **5**–**7** were carried out in boiling methylcyclohexane soln. Pure **5** or **6** (100 mg, 0.298 mmole) were refluxed for 5 hr. Removal of the solvent gave in both cases 92 mg (100%) crude solid which was recrystallized from CHCl$_3$/MeOH to give in both cases 87 mg (95%) of *cis,trans*- **8**: m.p. 208–214° (dec), PMR (CDCl$_3$) δ0.915 (s, 9, (CH$_3$)$_3$C−) δ0.95 (s, 9, (CH$_3$)$_3$C−), and δ1.0–2.2 (complex, 18, ring $\underline{H}$), mass spectrum *m/e* 308 (parent). (Found: C, 77.48; H, 11.72; S, 10.28. Calc. for C$_{20}$H$_{36}$S: C, 77.85; H, 11.76; S, 10.39%).

The crude pyrolysis mixtures from both **5** and **6** before recrystallization were carefully monitored by NMR in the t-Bu region and no trace of a third t-Bu peak could be found. NMR spectra before and after recrystallization were identical.

For preparative purposes unseparated mixtures of **5**/**6** were used. Product **8** is formed exclusively and in quantitative yield.

Pyrolysis of **7** (100 mg, 0.98 mmole) under the same conditions gave after removal of the solvent 92 mg (100%) of crude product, which after recrystallization from CHCl$_3$/MeOH gave 80 mg (0.257 mmole, 86%) of *cis,cis*- **9**: m.p. 224–228° (dec), PMR (CDCl$_3$) δ0.90 (s, 18, (CH$_3$)$_3$C−), δ1.0–2.3 (complex, 18, ring H), mass spectrum *m/e* 308 (parent). The t-Bu absorption region in the PMR spectrum was carefully monitored using wide sweep widths to try to find indications for a more t-Bu absorptions: none were forthcoming. Spectra before and after recrystallization were unchanged. Conditions were developed for separation of **8** and **9** (silica gel on aluminum oxide using CH$_2$Cl$_2$/C$_6$H$_2$). Both isomers gave only single spots under these conditions. PMR data for the thiiranes are given in Table 1.

If intended for further synthetic purposes the thiiranes were not recrystallized. Some experience is necessary to obtain the proper CHCl$_3$/MeOH mixture (roughly 50:50) for recrystallization; if the volume becomes too great (the thiiranes are very poorly soluble in MeOH) low recovery results.

Desulfurization of **8** *and* **9** was investigated using various reagents; the following conditions are in our opinion optimal. A soln of **8** (650 mg, 2.11 mmole) in *ca.* 20 ml xylene and *tri*-butylphosphine (452 mg, 2.24 mmoles) was added. The soln was refluxed vigorously for 5 hr. The solvent was removed under vacuum and the residue was chromatographed over flurosil using cyclohexane as eluent. The first 100 ml of soln were collected, the solvent was removed, and the white solid remaining was recrystallized from MeOH/CHCl$_3$ to give 400 mg (1.45 mmole, 69%) of *anti*- **11**; m.p. 183–183.5°, PMR (CCl$_4$) δ0.84(s, 18, (CH$_3$)$_3$C−), δ1.0–2.0 (complex, 14, ring H), and δ2.67 (broad d, 4, J = *ca.* 12.5 Hz, allylic $\underline{H}_e$); mass spectrum *m/e* 276 (parent). The ^{13}C spectrum is given in Table 1. (Found: C, 86.58; H, 13.15. Calc. for C$_{20}$H$_{36}$; C, 86.85; H, 13.15%).

A soln of **7** (2.0 g, 5.95 mmole) was refluxed in methylcyclohexane for 6 hr. The solvent was removed and the crude solid without any work-up was dissolved in *ca.* 20 ml xylene. Tributylphosphine (1400 mg, 6.92 mmole) was added (equally good results are obtained with triphenylphosphine) and the solution was refluxed. Within 1 hr TLC controls showed complete conversion to olefin. Reflux was continued 2–3 hr more. The solvent was removed and the crude residue was chromatographed over *ca.* 150 g silica gel using cyclohexane as eluent. The first 250 ml soln were collected, the solvent was removed, and the residue recrystallized from MeOH/CHCl$_3$ to give 1350 mg (4.90 mmole, 82%) of *syn*- **12**; m.p. 137–138.5°, PMR (CCl$_4$) δ0.87 (s, 18, (CH$_3$)$_3$C−), δ1.0–2.0 (complex, 14, ring $\underline{H}$), and δ2.67 (broad d, 4, J = *ca.* 12.5 Hz, allylic $\underline{H}_e$); mass spectrum *m/e* 276 (parent). The ^{13}C spectrum is given in Table 1. (Found: C, 86.83; H, 13.26. Calc. for C$_{20}$H$_{36}$: C, 86.85; H, 13.15%).

Attempts to prepare **11** by desulfurization of **8** with triphenylphosphine in refluxing xylene led to only slight reaction after 24 hr. Desulfurization could be accomplished by heating a melt of **8** with triphenylphosphine in a Bunsen burner flame. Desulfurization is clean but experimentally difficult owing to sublimation of **8**.

In all cases the t-Bu regions of the NMR spectra of crude olefin products before recrystallization were examined but no trace of extra t-Bu absorptions could be found.

Pinacol dimerization of 4-t-butylcyclohexanone.[17] A soln of 4-t-butylcyclohexanone (45 g, 292 mmole) in dry benzene (30 ml) was added slowly and with care to a vigorously stirred dry benzene soln (100 ml) containing Al powder (17.5 g, 650 mmole) and mercuric chloride (7 g, 25.8 mmole) at reflux. Addition of ketone was started as soon as the aluminium amalgam soln become dark green and began to smoke. A vigorous reaction took place on addition of ketone. After completing of addition reflux was continued 40 min and then after cooling in ice a mixture of benzene (150 ml) and water (85 ml) was added with care. The benzene was separated, washed with water, and dried over $MgSO_4$. Partial removal of the solvent and cooling gave a crude mixture of glycols (9.40 g, 30.3 mmole, 21%). No attempt was made to improve the yield.

Recrystallization from MeOH gave white crystals, which were recrystallized a second time to give 3.86 g pure *cis*- **16**: m.p. 174–177.5°, PMR (C_6D_6) δ (s, 18, $(CH_3)_3C$) and δ 1.3–1.7 (complex, 18, ring H); IR (KBr) 3610 (sharp), 3460 (broad), 2940, 2860, 1440, 1360, 1300, 1230, 1175, 1105, 1040, 970, 905 and 860 cm^{-1}. The ratio of the 3610 cm^{-1} to the 3640 cm^{-1} peak decreased as the concentration of **4** was increased. Measurements were made at four different concentrations in KBr (attempts to use a solvent were frustrated by the insolubility of the compound). Mass spectrum *m/e* 306 parent. The parent peak was too weak to permit exact mass measurement (*m/e* 153 is 100% peak). (Found: C, 77.24; H, 12.34. Calc. for $C_{20}H_{38}O_2$: C, 77.34; H, 12.36%).

The mother liquors from the above reaction were concentrated and the solid obtained was recrystallized 3 × from MeOH to give *ca.* 1 g *trans*- **17**; m.p. 252–255°, PMR (C_6D_6) δ0.90 (s, 18, $(CH_3)_3C$) and δ 1.3–1.7 (complex, 18, ring $\underline{H}$), IR (KBr) 3600 (small sharp shoulder), 3500 (broad), 2940, 2860, 1362, 1230, 1885 and 940 cm^{-1}. The 3600 cm^{-1} absorption underwent no detectable change in intensity relative to the 3500 cm^{-1} absorption in the same concentration range as used with **16**. Mass spectrum *m/e* 306 parent. The same problems as with **16** were encountered on attempted exact mass measurement.

Recovery of the mother liquors and repeated recrystallization from benzene gave *ca.* 100 mg trans- **18**; m.p. 185–188°, PMR (C_6D_6) δ0.85 (s, 9, $(CH_3)_3C$–), δ0.88 (s, 9, $(CH_3)_3C$–), and δ 1.3–1.7 (complex, 18, ring $\underline{H}$); IR (KBr) 3610 (weak shoulder, sharp), 3450 (very broad), 2950, 2870, 1435, 1395, 1363, 1240 and 947 cm^{-1}. The 3610 cm^{-1} absorption underwent no detectable change in intensity relative to the 3450 cm^{-1} absorption in the same concentration range as used with **16**. Mass spectrum *m/e* 306 parent (very weak, *m/e* 153 100%). Attempts to obtain an exact mass measurement were unsuccessful.

Hydroxylation of **11** *and* **12** were carried out using standard procedures.[18] A suspension of **11** (131 mg, 0.474 mmole) in dioxane (5 ml) was added to OsO_4 (170 mg, 0.67 mmole) in 5 ml dioxane at room temp. The soln was stirred for 90 hr after which time H_2S was passed through the soln. The black solid was filtered off, and the dioxane was removed to give 150 mg (0.483 mmole, >100%) white crystals with spectra completely identical to those of **18** isolated previously. Two recrystallizations from MeOH gave material, m.p. 185–188°.

Exactly the same procedure was followed with **12**, which is more soluble in dioxane. There was obtained after work-up as above 150 mg (>100%) of a 70:30 mixture of **16**:**17** as determined by analysis of the PMR spectra of the crude reaction mixture.

Cycloadditions of **5–7** *with dimethylazodicarboxylate.* The following general procedure was used; the thiadiazoline (300 mg, 0.89 mmole) was dissolved in *ca.* 20 ml methylcyclohexane. This soln was added slowly (2–3 hr) to a refluxing soln of dimethyl azodicarboxylate (650 mg, 4.5 mmole) in 20 ml methylcyclohexane. After one night refluxing the solvent was removed and the residue was dissolved in ether and washed with 10% $NaHSO_3$ aq until colorless, and thereafter 1× with water followed by drying over $MgSO_4$.

Recrystallization from MeOH of the products from **5** and **6** gave in both cases 280 mg (0.617 mmole, 69%) of *trans,trans*- **19** or *cis,cis*- **20**; m.p. 148–152°, PMR (CCl_4) δ0.93 (s, 18, $(CH_3)_3C$–), δ0.9–3.2 (complex, 18, ring-$\underline{H}$), and δ3.71 (s, 6, $-OCH_3$); mass spectrum *m/e* 454 (parent). PMR spectra of crude reaction mixtures showed, on the basis of t-Bu absorptions, that the product consisted of minimally 90% **19/20**. The CMR spectra of **19/20** are given in Table 1. A sample of **19/20** (227 mg, 0.5 mmole) was dissolved in chloroform (10 ml) and cooled in an ice bath. A soln of *meta*-chloroperbenzoic acid (100 mg, 0.5 mmole) in 5 ml chloroform was added slowly with stirring. There was obtained 200 mg (0.425 mmole, 85%) of *trans,trans* or *cis,cis* - 3,11 - di|1,1 - dimethyl| - 14,15 - di-(methoxycarbonyl) - 14,15 - diaza - 7 - thiadispiro[5.1.5.2]pentadecane - 7 - oxide, m.p. 164–167° (from MeOH); PMR ($CDCl_3$) δ0.84 (s, 18, $(CH_3)_3C$), δ0.92–2.65 (complex, 18, ring $\underline{H}$), and δ3.72 (s, 6, OCH_3); IR (neat) 1740, 1720 (C=O), and 1060 cm^{-1} (S=O). Spectra take at 100 MHz failed to give any further resolution for the spectrum; the t-Bu and Me absorptions remained singlets. (Found: C, 61.00; H, 9.11; N, 5.90; S, 6.86. Calc. for $C_{24}H_{42}O_5N_2S$: C, 61.23; H, 9.01; N, 5.95; S, 6.81%).

From **7** there was obtained after separation by preparative layer chromatography on silica gel using benzene/ether 280 mg (70%) of *cis,trans*-**21** as a heavy oil, which crystallized slowly, m.p. 164–168°, PMR (CCl_4) δ0.85 (broad singlet, 18 two sets of $(CH_3)_3C$–), δ0.8–3.3 (complex, 18, ring $\underline{H}$), δ3.59 (s, 3, OCH_3) and δ3.61 (s, 3, OCH_3); IR (KBr) 2975, 2860 (C–H), 1725 (C=O), exact mass *m/e* 454.280719, Calc. 454.286510; the ^{13}C spectrum is given in Table 1.

Cycloadditions of **5–7** *with dimethyl acetylenedicarboxylic acid.* The same procedure and amounts as used with dimethyl azodicarboxylate were used. Work-up involved extraction of the crude cycloaddition products with n-pentane leaving the greater part of the excess dipolarophile, which is essentially insoluble in this reagent. From **5** and/or **6** there was obtained after separation from thiirane (**9**) by preparative layer chromatography 200 mg (0.445 mmole, 50%) of *trans,trans*- or *cis,cis* - 3,11 - di - [1,1 - dimethylethyl] - 14,15 - di(methoxycarbonyl) - 7 - thiadispiro[5.1.2]pentadeca - 14 - ene, m.p. 146–149°, PMR (CCl_4) δ0.91 (s, 18, $(CH_3)_3C$–), δ0.9–2.0 (complex, 18, ring-$\underline{H}$) and δ3.81 (s, 6, $-OCH_3$); IR (KBr) 1700 (C=O) and 1620 cm^{-1} (C=C); ^{13}C ($CDCl_3$) relative to TMS δ63.4 ($\underline{C}_\alpha$), δ39.6 ($\underline{C}H_{2\beta}$), δ24.7 ($\underline{C}H_{2\gamma}$), δ46.7 ($\underline{C}H_\delta$), δ32.4 ($\underline{C}$ of t-Bu), δ27.5 ($\underline{C}H_3$ of t-Bu), δ 144.0 (alkylidene $\underline{C}$), and δ52.0 ($O\underline{C}\underline{H}_3$). Mass spectrum *m/e* 450 (parent). Satisfactory elemental analysis data were not obtained.

All attempts to obtain a cycloaddition product from **7** led only to the formation of thiirane (**8**) in at least 95% yield.

Acknowledgements—We are grateful to Drs. W. Mungall and M. P. Doyle of Hope College, Holland, Michigan and that institution for making possible that Judy Kaiser could participate in an undergraduate exchange program with this University. Drs. J. de Wit and J. L. Wieringa provided aid in the obtainment of ^{13}C and 100 MHz NMR spectra. Mr. J. Buter provided synthetic assistance at several stages. We are indebted to Prof. M. J. Janssen of this University for helpful discussions concerning theoretical aspects.

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