

# Retention of Configuration and *E/Z* Stereoselectivity in the Photolysis of *cis*- and *trans*-Tetraalkyl-4-methylene-1-pyrazolines<sup>1,2)</sup>

Helmut Quast\* and Harald Jakobi

Institut für Organische Chemie der Universität Würzburg,  
Am Hubland, W-8700 Würzburg

Received January 2, 1991

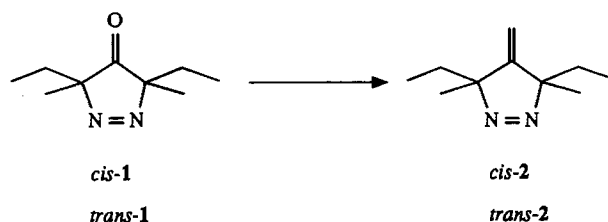
**Key Words:** 4*H*-Pyrazoles, 3,3,5,5-tetraalkyl-3,5-dihydro-4-methylene- / Cyclopropanes, 2,2,3,3-tetraalkyl-1-methylene- and 2,2-dialkyl-1-alkylidene- / Photolysis / Extrusion of molecular nitrogen / Configuration, retention of / *E/Z* Stereoselectivity / Trimethylenemethanes, bis-orthogonal and mono-orthogonal

The isomeric 4-methylene-1-pyrazolines *cis*- and *trans*-**2** are synthesized by a Wittig reaction from the pyrazolin-4-ones *cis*- and *trans*-**1**, respectively. Direct irradiation with 350-nm light of *cis*-**2** affords the alkylidenecyclopropanes *cis*-**8**, (*E*)- and (*Z*)-**9** (64:17:19) besides molecular nitrogen and small amounts of the 4-methylenepyrazolidine *cis*-**7** as a result of photoreduction. Under the same conditions, *trans*-**2** is converted into *trans*-**8** as well as (*E*)- and (*Z*)-**9** (64:14:22). The configurations of *cis*- and *trans*-**8** have been established by means of a 1,3-dipolar cycloaddition with mesityl nitrile oxide which furnishes two cycloadducts from *cis*-**8**, e.g. *cis*-**14A** and **B**, but only one cycloadduct from *trans*-**8**, viz. *trans*-**14**. The configurations of (*E*)- and (*Z*)-**9** have been assigned on the basis of homoallylic <sup>1</sup>H,<sup>1</sup>H coupling constants and nuclear Overhauser

experiments. The results demonstrate that, on the least-motion paths leading to *cis*- and *trans*-**8**, the configuration of the ring substituents in *cis*- and *trans*-**2** is completely retained. Of the non-least-motion products (*E*)- and (*Z*)-**9** the latter is favoured regardless of the configuration of the precursors *cis*- and *trans*-**2** though the extent of (*Z*) selectivity depends on that configuration. The results are interpreted in terms of bis-orthogonal trimethylenemethane diradicals as primary intermediates from which irreversible paths bifurcate. Cyclization yields *cis*-**8** (from *cis*-**2**) or *trans*-**8** (from *trans*-**2**) and 90°-bond rotations afford two diastereomeric mono-orthogonal trimethylenemethane diradicals [(*E*)- and (*Z*)-**18**] which eventually cyclize to the corresponding non-least-motion products (*E*)-**9** and (*Z*)-**9**.

For a long time, stereochemical evidence has contributed significantly to the elucidation of chemical reaction pathways<sup>3</sup>. In particular, the extent of retention of configuration has served as a demanding criterion for the distinction of one-step from two-step cycloaddition and cycloreversion reactions. Retention of configuration has been associated with either concertedness or two-step reactions via intermediates which cyclize very fast compared to the rate of bond rotation<sup>4</sup>. Van Auken and Rinehart, Jr., were the first to apply this criterion to the photoextrusion of molecular nitrogen from *cis/trans*-isomeric 1-pyrazolines and observed a preference for retention of configuration in the cyclopropane products<sup>5</sup>. Bartlett and Porter studied the stereochemical consequences of the photoextrusion of an azo group from a six-membered ring<sup>6</sup>. An excellent review by Givens summarizes the stereochemical results of the photoextrusion of small molecules<sup>7</sup>. No attention, however, has been paid as yet to the steric course of ring closure following the loss of molecular nitrogen from 4-alkylidene-1-pyrazolines. This is all the more surprising as their thermolysis and photolysis have been thoroughly studied in numerous investigations<sup>8–12</sup> which have received additional impetus from the interest in trimethylenemethane diradicals<sup>13</sup>. We now report that the photolysis of diastereomeric 4-methylene-1-pyrazolines (*cis*- and *trans*-**2**) yields methylenecyclopropanes (i.e. the least-motion products<sup>14</sup>) *cis*- and *trans*-**8**, respectively) with retention of configuration, while alkylidenecyclopro-

panes [viz. the non-least-motion products (*E*)-**9** and (*Z*)-**9**] are formed with different preferences for the (*Z*) diastereomer, depending on the configuration of the starting material.



## Synthesis of *cis*- and *trans*-Tetraalkyl-4-methylene-1-pyrazolines

The major obstacle to a stereochemical study of the nitrogen extrusion from 4-methylene-1-pyrazolines was recently overcome by the synthesis of both diastereomeric pyrazolinones *cis*-**1** and *trans*-**1** in satisfactory quantities with a diastereomeric excess of at least 99%<sup>15</sup>. While the tetramethyl-4-methylene-1-pyrazoline **3** could be obtained conveniently by a Wittig reaction from the corresponding ketone<sup>16–18</sup>, the diethyl dimethylpyrazolinones *cis*- and *trans*-**1** reacted too sluggishly under the same conditions. Even prolonged heating with an excess of the phosphorus ylide in ether in sealed tubes to temperatures as high as 100°C did

not result in complete conversions. Eventually, the goal was achieved by a change to refluxing toluene as solvent. Thus, the 4-methylene-1-pyrazolines *cis*- and *trans*-**2** were obtained in 74 and 68% yield, respectively, as colourless liquids which were characterized by analytical and spectroscopic methods (Tables 2 and 3). The ethyl protons of both *cis*- and *trans*-**2** constitute ABX<sub>3</sub> spin systems which give spectra of higher order even at a spectrometer frequency of 400 MHz (Table 2).

## Methods

The diastereomeric purity of *cis*- and *trans*-**2** as well as the photolysis products was checked by NMR spectroscopy and by gas chromatography on a very efficient column. When the retention times differed too little to allow the detection of traces of the minor diastereomer, a singlet of the latter in the proton spectrum was compared to the carbon-13 satellites of the corresponding singlet of the major isomer. Thus, the limits of detection by proton spectroscopy (<0.5%) approached that of gas chromatography in the present study. For example, diastereomeric excesses of at least 99% were confirmed by NMR for both diastereomers *cis*- and *trans*-**2**, which corresponded to the diastereomeric purities of the starting ketones *cis*- and *trans*-**1** as expected.

Carefully degassed solutions of the 4-methylene-1-pyrazolines *cis*- and *trans*-**2** in [D<sub>6</sub>]benzene or [D<sub>12</sub>]cyclohexane, sealed in NMR sample tubes, were kept at 20–25 °C and irradiated through a 345-nm cut-off filter with a focussed high-pressure mercury lamp. The course of the photolyses was monitored by proton spectra which were complemented by carbon-13 spectra and gas chromatograms after termination of the irradiation. Proton spectroscopy and gas chromatography furnished virtually identical results (Table 1), except that gas chromatography found the amounts of photoreduction products (*cis*- and *trans*-**7**, see below) somewhat too low, most likely because of peak tailing and the neglect of differences in the response factors. The signals in the carbon-13 spectra were assigned on the basis of DEPT spectra. When several components were present in similar proportions as in the case of irradiated or thermally equilibrated samples, <sup>1</sup>H, <sup>1</sup>H decoupling experiments and <sup>1</sup>H, <sup>13</sup>C COSY spectra allowed an unequivocal assignment of the signals to a particular compound.

## Results

The irradiated solutions remained clear and colourless in all experiments, even till the photolyses had gone virtually to completion. The results, compiled in Table 1, were obtained after ten (for [D<sub>6</sub>]benzene solutions) or thirty hours of irradiation (for [D<sub>12</sub>]cyclohexane solutions), when almost quantitative (>98%) conversions were observed. While the amounts of both substrates, *cis*- and *trans*-**2**, decreased steadily during irradiation, their diastereomeric purity remained unchanged. There were no observable photochemical *cis* ⇌ *trans* conversions, neither between *cis*- and *trans*-**2** nor between the diastereomeric pairs of the products, viz. *cis*- and *trans*-**8** as well as (*E*)- and (*Z*)-**9**.

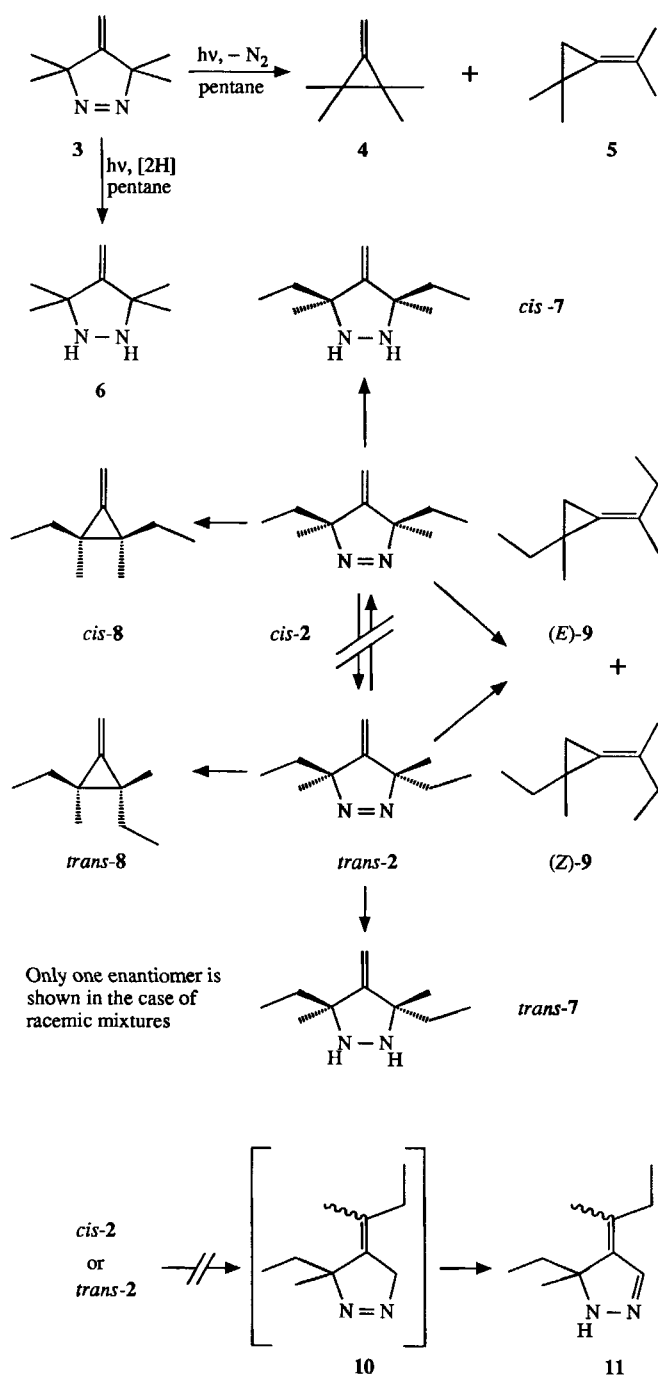
In a reinvestigation of the tetramethyl-4-methylene-1-pyrazoline **3**<sup>18</sup>, the novel photoreduction product **6** was detected besides the known alkylidenecyclopropanes **4** and **5**<sup>10,12,17</sup> provided that molecular oxygen was rigorously excluded and hydrogen donor solvents were employed. Therefore, formation of small amounts of the photoreduction products *cis*- and *trans*-**7** could be expected under the experimental conditions used in the present study. In fact, singlets of low intensity between δ = 4.5 and 4.7 in the proton spectra from irradiated solutions of *cis*-**2** and *trans*-**2** could be assigned to such photoreduction products by a comparison with the tetramethyl compound **6**<sup>18</sup>. However, rigorous proof of the structure and configuration of those minor products has not been attempted. Nevertheless, it seems safe to assume that the configurations of the precursors have not been inverted in the photoreduction process. The ratios of the nitrogen extrusion products and the photoreduction products are compiled in Table 1.

A recent study of the photolysis of **3** has uncovered traces of an isomer of type **11** (four methyl groups as substituents) which were interpreted in terms of a turnaround isomerization of **3** via diazenylallyl diradicals. The experimental result, claimed to solve the intriguing problem of one-bond versus two-bond cleavage in the photolysis of **3**<sup>12</sup>, not only met with scepticism<sup>19</sup>, but could not be confirmed<sup>18</sup>, unfortunately. Nevertheless, the proton spectra and gas chromatograms recorded after irradiation of *cis*- and *trans*-**2** were scrutinized for traces of the hypothetical isomers (*E*)- and (*Z*)-**11**, but without success.

The photoextrusion of molecular nitrogen from each diastereomer, *cis*- and *trans*-**2**, yields three products. The major product of *cis*-**2** differs from that of *trans*-**2**, but the two minor products, albeit being formed in somewhat different ratios, are the same for both precursors. A cursory inspection of the NMR spectra immediately revealed the methylenecyclopropane structure **8** for the major products and the alkylidenecyclopropane structure **9** for both minor products (Tables 2 and 3). Thus, the least-motion path affording **8** is followed with very high diastereospecificity whereas, on the non-least-motion path leading to **9**, different stereoselectivities are observed favouring the formation of the same diastereomer from *cis*- and *trans*-**2** as well.

The NMR arguments for the gross structures were corroborated by the results of equilibration experiments. To this end, the irradiated solutions were heated to 180.0 ± 0.2 °C till the proportions of the components did not change anymore. As could be expected from the thermal equilibration of **4** and **5** which resulted in an equilibrium concentration for **4** of only 0.16 ± 0.02% at 180.15 °C<sup>17</sup>) both major photoproducts (*cis*- and *trans*-**8**) were almost quantitatively converted into a mixture of the minor (but thermodynamically more stable) products [(*E*)- and (*Z*)-**9**] of the photolysis. Only traces of the predominant photoproducts were detected in the thermally equilibrated solutions. In addition, the ratio of the minor photoproducts, being different at the beginning of the thermal equilibration because *cis*- or *trans*-**2** was irradiated (Table 1), eventually attained the value of one. Taken together, these results left no room for any

doubts concerning the gross structures of the photolysis products.



The assignment of the configurations to the diastereomeric methylenecyclopropanes **8** presented a non-trivial problem which could not be solved unequivocally on the basis of NMR spectra, at least not those recorded in achiral solvents as in the present study. The addition of a reagent to the double bond of *trans*-**8** would produce a *single* (racemic) product, however, while *two diastereomeric* products are to be expected from *cis*-**8**. Because both *cis*- and *trans*-**8** were available only in solutions together with the alkylidene-cyclopropanes (*E*- and *Z*-**9**), a reagent was required

Table 1. Ratios of products obtained by irradiation through a 345-nm cut-off filter of the methylenepyzolines *cis*- and *trans*-**2** in hydrocarbon solvents

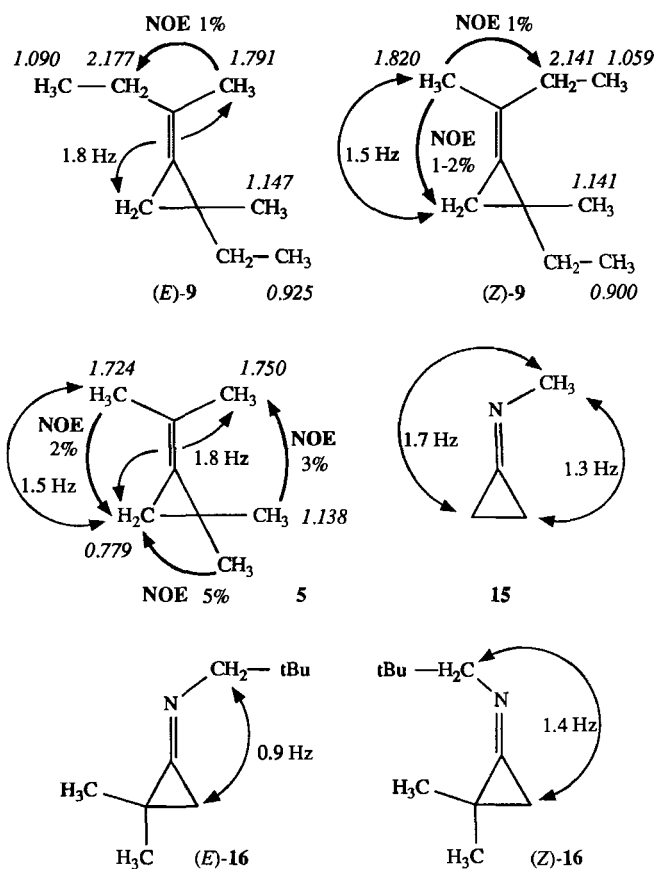
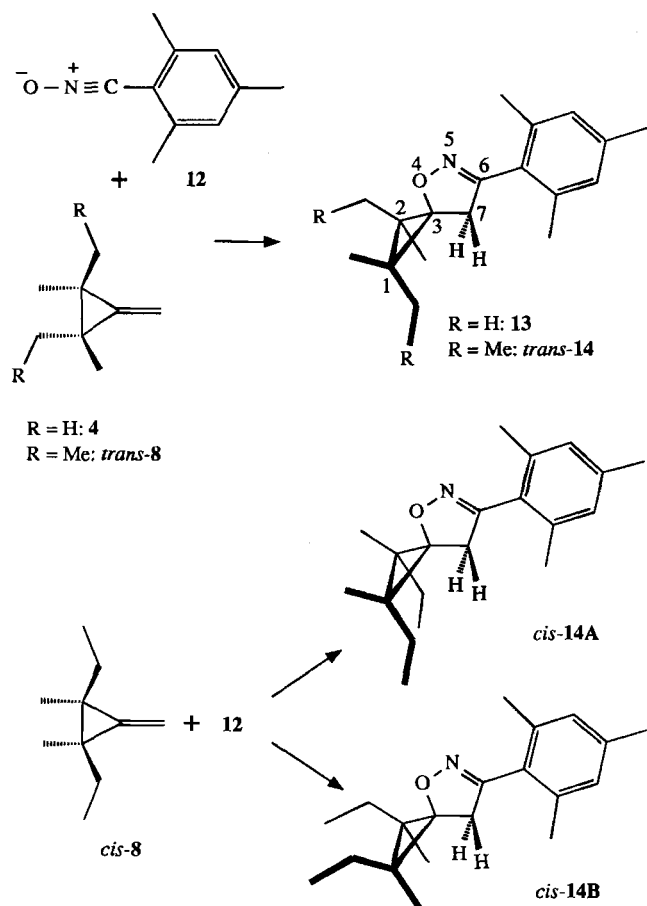
Solvent	(8 + 9) : 7 =		8 : 9	<i>cis</i> - <b>8</b> : <i>trans</i> - <b>8</b>	<i>E</i> - <b>9</b> : <i>Z</i> - <b>9</b>	Method of Analysis
	Extrusion of $N_2$ / Photoreduction <sup>a)</sup>					
Photolysis of <i>trans</i> - <b>2</b>						
$C_6D_6$	99 : 1 (99.4 : 0.6)		64 : 36 65 : 35	1 : 99	39 : 61 39 : 61	NMR GC
$C_6D_{12}$	93 : 7 (94 : 6)		63 : 37 64 : 36	1 : 99	39 : 61 39 : 61	NMR GC
Photolysis of <i>cis</i> - <b>2</b>						
$C_6D_6$	99 : 1 (99.3 : 0.7)		63 : 37 64 : 36	99 : 1	47 : 53 48 : 52	NMR GC
$C_6D_{12}$	95 : 5 (97 : 3)		64 : 36 65 : 35	99 : 1	48 : 52 48 : 52	NMR GC

<sup>a)</sup> The ratios given in brackets are regarded as less reliable, because the photoreduction products *cis*- and *trans*-**7** exhibited peak tailing in the gas chromatograms which was detrimental to the precision of the electronic integrations. Furthermore, differences in the response factors were neglected.

which would react rapidly in a well-defined manner and selectively with the (less substituted) double bond of the methylenecyclopropanes **8**. In addition, the products would have to be sufficiently stable and to allow ready identification by NMR spectroscopy. These requirements could not be expected to be met by most of the reagents which have hitherto been added to the double bond of methylenecyclopropanes<sup>20–23</sup>. For example, more complex proton spectra can be predicted for many products. The 1,3-dipolar cycloaddition of phenyl azide to the parent methylenecyclopropane is highly regioselective but requires several months<sup>21</sup>, and the cycloaddition of nitrones is neither reasonably regioselective<sup>22</sup> nor affords cycloadducts having simple proton spectra. Therefore, we turned to nitrile oxides as 1,3-dipoles, the [3 + 2] cycloaddition of which to the parent methylenecyclopropane has been reported to be sufficiently fast and highly regioselective<sup>23</sup>. In addition, several nitrile oxides, for example mesityl nitrile oxide (**12**), exist as moderately stable, ready-to-use reagents<sup>24,25</sup>. In fact, the 1,3-dipolar cycloaddition of **12** to the methylenecyclopropane **4** proceeded smoothly at temperatures as low as 20–80°C affording a single product in virtually quantitative yield, viz. the spirocyclic isoxazoline **13**, which formed colourless crystals melting at 53–54°C. The expected<sup>23</sup> structure **13** was confirmed by analytical and spectroscopic techniques (Tables 2 and 3). Most significantly, the singlet of the methylene protons appeared at rather low field ( $\delta = 2.67$  in  $[D_6]$ benzene, 2.88 in  $[D_{12}]$ cyclohexane), and was, therefore, well separated from the resonance lines of the methyl and ethyl groups attached to a cyclopropane ring or a carbon-carbon double bond as in (*E*- and *Z*-**9**). Thus, the signals of the isoxazoline ring protons offer an excellent criterion for an unequivocal assignment of the configurations to the least-motion photoproducts of *cis*- and *trans*-**2**.

To this end, the mixtures of photoproducts obtained from *cis*-**2** and *trans*-**2** were allowed to react with mesityl nitrile

oxide (**12**). In  $[D_6]$ benzene solutions at room temperature and in  $[D_{12}]$ cyclohexane solutions at  $50^\circ\text{C}$ , the methylenecyclopropanes *cis*- and *trans*-**8** slowly turned into products which exhibited proton signals in the same range as did the spirocyclic isoxazoline **13** ( $\delta = 2.6 - 2.9$ ). When the sequence of events had started from *cis*-**2**, two singlets (ratio 63:37 in both solvents) appeared which were assigned to the diastereomeric [3 + 2] cycloadducts *cis*-**14A** and *cis*-**14B**. Most probably, the major isomer possesses structure *cis*-**14A** because the methyl groups at the cyclopropane ring of *cis*-**8** encumber the approach of the 1,3-dipole less than the ethyl groups do. The formation of two products was also shown by the carbon-13 spectrum. On the other hand, *trans*-**2** yielded in the same sequence of reactions only a single product. The AB pattern observed in its proton spectrum proved the non-equivalence of the ring methylene protons and hence the structure *trans*-**14**. The carbon-13 spectrum confirmed that only one product had been formed in the 1,3-dipolar cycloaddition reaction with mesityl nitrile oxide. Though isolation of the spirocyclic isoxazolines *cis*-**14A**, *cis*-**14B** and *trans*-**14** in a pure state was not attempted, their structures could be established by the proton and carbon-13 spectra (Tables 2 and 3). These results prove beyond any doubt that, on photoextrusion of molecular nitrogen, *cis*-**2** affords only *cis*-**8**, and *trans*-**2** yields only *trans*-**8**. Thus, product formation occurs on the least-motion path with retention of configuration. If there is any stereo-randomization, it certainly amounts to less than 1%.



Proton chemical shifts ( $\delta$ , in italics), absolute values of long-range coupling constants [Hz] and nuclear Overhauser enhancements

The configurations of the diastereomeric alkylidenecyclopropanes **9** are derived by means of long-range effects observed in the proton spectra. The isopropylidenecyclopropane **5** could serve as a reference since its spectrum had recently been reinvestigated under conditions of high resolution<sup>18</sup>. The analysis of the proton spectrum of **5** had revealed a small difference in the *cisoid* and *transoid* homoallylic coupling constants which were hitherto either not resolved or regarded as identical<sup>26</sup>, or not assigned in similar alkylidenecyclopropanes<sup>27</sup>. Such differences in the *cisoid* and *transoid* homoallylic coupling constants are well known from the cyclopropanimines **15**<sup>28</sup> and (*E*)- and (*Z*)-**16**<sup>29</sup>. According to the useful rule that  $^5J_{transoid}$  is larger than  $^5J_{cisoid}$ <sup>30</sup>, the multiplet of the allylic methyl protons, exhibiting the larger homoallylic coupling constant, was assigned to (*E*)-**9** and the other multiplet was attributed to (*Z*)-**9**. This assignment was corroborated by nuclear Overhauser enhancement experiments<sup>31</sup> which showed small but significant effects as in the study of **5**<sup>18</sup>. Hence, the predominant alkylidenecyclopropane formed by photoextrusion of molecular nitrogen from both *cis*-**2** and *trans*-**2** is (*Z*)-**9** and the minor isomer is (*E*)-**9** (Table 1).

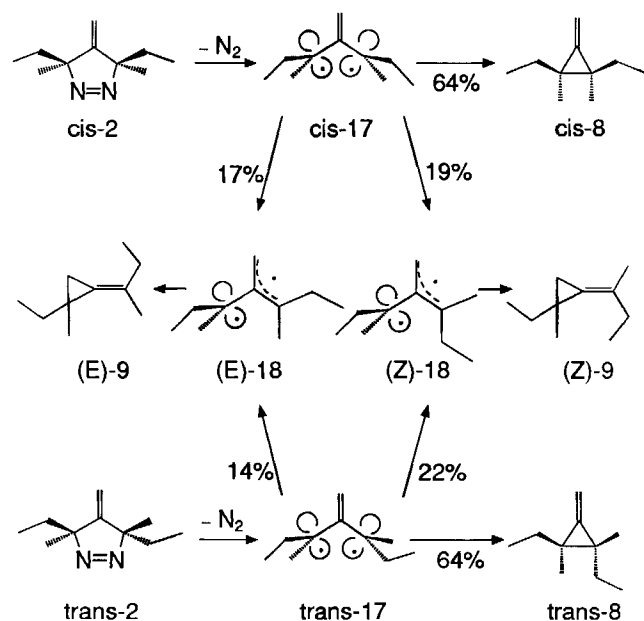
## Discussion

The direct irradiation of *cis*-**2** and *trans*-**2** results predominantly in the extrusion of molecular nitrogen. Photore-

duction is only a minor pathway. The regioselectivities of product formation, viz. the ratios of **8** and **9**, are somewhat larger than that observed in the photolysis of **3**, i.e. **4**:**5** = 57:43<sup>17</sup>, 52:48<sup>10</sup>, (55 ± 1):(45 ± 1)<sup>18</sup>. This comparison shows that an increase in the size of the ring substituents of 4-methylene-1-pyrazolines favours the least-motion product regardless of the relative configuration of the ring substituents. This conclusion is in accordance with the trend in the photolysis of 4-alkylidene-tetramethyl-1-pyrazolines which favours the least-motion products when the number or the size of the substituents at the double bond is increased<sup>10</sup>.

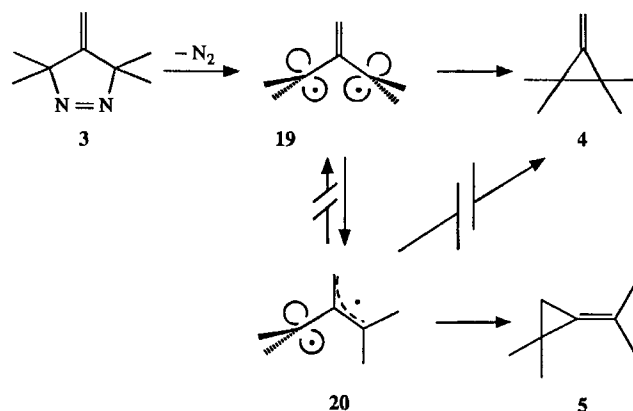
The most important result of the present study is the retention of configuration of the substrates *cis*-**2** and *trans*-**2** in the methylenecyclopropanes *cis*-**8** and *trans*-**8**. Formation of the latter from the mono-orthogonal trimethylenemethanes **18** cannot be expected to be stereoselective let alone completely stereoselective. This argument excludes the mono-orthogonal trimethylenemethanes **18** as possible precursors. It is in perfect agreement with the working hypothesis involving primary formation of bis-orthogonal trimethylenemethane diradicals as invoked by Bushby and coworkers<sup>10</sup> (i.e. *cis*-**17** and *trans*-**17**) but argues against an equilibration between bis-orthogonal and mono-orthogonal trimethylenemethanes [viz. (*E*)-**18** and (*Z*)-**18**]. Rather, the 90° bond rotations of the former yielding the latter must be irreversible, probably because the 90° rotation of the methylene group and ring closure to the thermodynamically favoured alkylidenecyclopropanes (*E*)-**9** and (*Z*)-**9** are fast events. Therefore, the observed ratio of least-motion to non-least-motion products can be related directly to the relative propensities for cyclization and 90° bond rotation in the bis-orthogonal trimethylenemethanes.

The non-least-motion products (*E*)-**9** and (*Z*)-**9** are formed with modest degrees of diastereoselectivity which are different as *cis*-**2** and *trans*-**2** was photolyzed. This difference is, of course, not compatible with an equilibrium between the mono-orthogonal trimethylenemethanes (*E*)- and (*Z*)-**18**.



Starting from both methylenepyrazolines, formation of (*Z*)-**9** is somewhat preferred over that of (*E*)-**9**. For *trans*-**2**, possessing C<sub>2</sub> symmetry, the (*Z*) preference can be traced back to subtle differences between the 1,3-interactions in (*E*)- and (*Z*)-**18**. In the case of *cis*-**2**, the influence of the intrinsic relative stabilities of (*E*)- and (*Z*)-**18** is modified by the stronger propensity of the ethyl groups, being at the same side in *cis*-**17**, to rotate away from each other.

In summary, the results of the present study allow to draw the mechanistic pictograph for product formation in the photolysis of 4-methylene-1-pyrazolines with more precision than has hitherto been possible. For the sake of simplicity, the most plausible working hypothesis is exemplified for the tetramethyl-4-methylene-1-pyrazoline **3**. As strongly advocated by Bushby and coworkers<sup>10</sup>, the bis-orthogonal trimethylenemethane **19** is the key intermediate from which the least-motion path and the non-least-motion path bifurcate. There is no equilibrium between the diastereomeric trimethylenemethanes **19** and **20** nor is the least-motion product **4** formed from the latter. Thus, the observed ratio of **4** to **5** simply reflects the relative rates of cyclization and bond rotation in the bis-orthogonal trimethylenemethane **19**.



The authors express their gratitude to Professor *M. Christl* for valuable hints and a gift of mesityl nitrile oxide (**12**). We are grateful to Professor *P. Binger*, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, for a gift of 1,1,2,2-tetramethyl-3-methylenecyclopropane (**4**). We thank Mrs. *E. Ruckdeschel* and Dr. *D. Scheutzw* for performing the NMR spectra and the NOE experiments, Dr. *G. Lange* and Mr. *F. Dadrich* for recording the mass spectra. Financial support by the *Fonds der Chemischen Industrie* is gratefully acknowledged. H. J. thanks for a doctoral fellowship donated by the *Freistaat Bayern*.

## Experimental

Results of the photolysis experiments: Table 1; <sup>1</sup>H NMR: Table 2; <sup>13</sup>C NMR: Table 3. — Melting points: Sealed capillary tubes, Büchi apparatus. — NMR: Bruker WM 400 spectrometer, PFT mode (pulse angle 20–35°). The deuterium solvent signal was used as an internal lock. The spectral windows were carefully chosen to ensure that folding did not obscure the spectral region of interest, while at the same time giving a digital resolution in the frequency domain of better than 0.08 Hz. Zero-filling to 64 K data points was carried out before the Fourier transformation<sup>32</sup>. In order to achieve

Table 2. Chemical shifts ( $\delta$  values relative to internal tetramethylsilane) and absolute values of coupling constants [Hz] in 400-MHz proton spectra. The signals are singlets unless specified otherwise

Cpd.	=CH <sub>2</sub>	CH <sub>3</sub>	(dq) CH <sub>2</sub>	— CH <sub>3</sub> (t)	<sup>2</sup> J	<sup>3</sup> J	a)
cis-2	4.628	1.196	1.534 1.763	0.849	14.0	7.5	B
	4.840	1.269	1.621 1.850	0.895	13.9	7.5	C
trans-2	4.622	1.231	1.462 1.881	0.700	13.9	7.5	B
	4.844	1.286	1.586 1.950	0.751	13.9	7.5	C
cis-7 <sup>b)</sup>	4.561						B
	4.675						C
trans-7 <sup>b)</sup>	4.568						B
	4.689						C
cis-8	5.278	1.131	1.466 1.487	0.968	14.0	7.5	B
	5.117	1.123	1.473 <sup>e)</sup>	0.964		7.4	C
trans-8	5.266	1.138	1.428 1.510	0.950	14.0	7.4	B
	5.099	1.130	1.421 1.498	0.962	14.2	7.4	C
	>CH <sub>2</sub> (m)	CH <sub>3</sub> — C — CH <sub>2</sub>	— CH <sub>3</sub> (t)				
(Z)-9 <sup>d)</sup>	0.73 - 0.77 0.84 - 0.88	1.141	1.29 - 1.57	0.900		7.4	B
	0.64 - 0.68 0.73 - 0.77	1.113	1.28 - 1.56	0.889		7.4	C
(E)-9 <sup>d)</sup>	0.84 - 0.88 0.92 - 0.96	1.147	1.29 - 1.57	0.925		7.4	B
	0.73 - 0.79 0.82 - 0.86	1.109	1.28 - 1.56	0.908		7.4	C
	<sup>4</sup> J	<sup>5</sup> J	(tt) CH <sub>3</sub> — C — CH <sub>2</sub>	— CH <sub>3</sub> (t)			
(Z)-9	0.4	1.5	1.820	2.141 <sup>e)</sup>	1.059		7.5 B
	0.4	1.5	1.738	2.113 <sup>e)</sup>	1.028		7.5 C
(E)-9	0.4	1.8	1.791	2.177 <sup>e)</sup>	1.090		7.5 B
	0.4	1.8	1.749	2.113 <sup>e)</sup>	1.039		7.5 C
	Cyclopropane Substituents				Mesityl Group <sup>d)</sup>		
	CH <sub>3</sub>	(m) CH <sub>2</sub> <sup>g)</sup>	— CH <sub>3</sub> (t)	<sup>3</sup> J	H <sub>2</sub> C(7)	CH <sub>3</sub>	CH
12						1.944 1.893	6.379 B
						2.332 2.230	6.800 C
13	0.825 1.260				2.670 (s)	2.152 2.112	6.712 B
	0.978 1.159				2.884	2.167 2.218	6.770 C
cis-14 <sup>h)</sup>	0.832 1.237	1.11 - 1.21 1.72 - 1.80	1.017 0.878	7.4 7.4	2.664 (s) 2.705 (s)	2.165 2.114 2.180	6.712 B
	0.969 1.133	1.15 - 1.32 1.60 - 1.70	0.956	7.4	2.873 (s) 2.900 (s)	2.165 2.207	6.762 C 6.753
trans-14	0.986 1.175	1.12 - 1.43 1.46 - 1.70	0.941 0.952	7.4 7.4	2.851 <sup>i)</sup> 2.890	2.150 2.202	6.781 C

<sup>a)</sup> Solvent B: [D<sub>6</sub>]benzene, C: [D<sub>12</sub>]cyclohexane. — <sup>b)</sup> *cis*- and *trans*-7 were available only as minor components in mixtures with *cis*- and *trans*-8, respectively, and (*E*)- and (*Z*)-9. Because of extensive overlap, only the signals of the exocyclic methylene protons could be identified. — <sup>c)</sup> The diastereotopic methylene protons resonate

at the same frequency. — <sup>d)</sup> Mixtures of the diastereomers (*E*)- and (*Z*)-9. The ABX<sub>3</sub> spectra of the ethyl groups at the cyclopropane rings could not be analysed completely because of overlap of the AB parts. — <sup>e)</sup> The quartet shows further but poorly resolved splittings by long-range couplings. — <sup>f)</sup> Some signals of the mesityl group could not be identified because of signal overlap. The numbers given in the first place refer to the more intense signal. — <sup>g)</sup> The ABX<sub>3</sub> spectra of the ethyl groups at the cyclopropane rings could not be analysed completely because of overlap of the AB parts with signals of (*E*)- and (*Z*)-9. — <sup>h)</sup> Mixtures of *cis*-14A (= major isomer) and *cis*-14B. The numbers given in the first place refer to the more intense signal. — <sup>i)</sup> The diastereotopic protons constitute an AB spin system, <sup>2</sup>J<sub>AB</sub> = 17.3 Hz.

resolution of very close signals and of small long-range couplings, we carried out a Lorentzian-to-Gaussian line-shape transformation<sup>32</sup>. Spectra of higher order were analysed by standard methods<sup>33</sup> and simulated with the help of the program RACON<sup>34</sup>. The samples used in the NOE experiments were carefully degassed by several freeze-pump-thaw cycles and sealed under high vacuum (10<sup>-5</sup> Torr). — IR: Perkin-Elmer 1420 spectrometer. — Low-resolution 70-eV MS: Finnigan MAT 8200, connected to an SS 200 data system. — The exact mass of 13 was determined by means of a Finnigan MAT 90 high-resolution mass spectrometer and perfluorokerosine calibration. — Gas chromatography: Packard model 436 chromatograph, equipped with a Shimadzu Chromatopac C-R6A integrator. A 50 × 0.0001 m fused-silica column having 425 500 theoretical plates was employed, which was coated with 0.12 μm silicon oil CP Sil 5CB; 4.0 bar N<sub>2</sub> pressure, split injection 1:50, column temperature C = 100°C, t<sub>R</sub>[min] = 32.56 (*cis*-2), 32.75 (*trans*-2), separation factor α = 1.006; C: 20 min at 150°C, with 5°C/min to 180°C, t<sub>R</sub>[min] = 13.23 (*cis*- and *trans*-8), 13.58 [(*E*)-9], 13.93 [(*Z*)-9], 28.20 (*cis*-2), 28.28 (*trans*-2), 30.83 (*cis*- and *trans*-7).

Toluene was distilled under argon (99.998%) from sodium hydride. A sample of 1,1,2,2-tetramethyl-3-methylenecyclopropane (4)<sup>35</sup> was a gift by Prof. P. Binger, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr. Mesityl nitrile oxide (12)<sup>25,36</sup> was donated by Prof. M. Christl, University of Würzburg. Recrystallization from methanol<sup>25</sup> afforded beige needles, m.p. 110–111°C (ref.<sup>25</sup> 110–112°C). The pyrazolinones *cis*- and *trans*-1 were prepared as described previously<sup>19</sup>.

*r*-3,5-Diethyl-3,5-dihydro-*t*-3,5-dimethyl-4-methylene-4H-pyrazole (*cis*-2): A suspension of 7.14 g (20 mmol) of methyltriphenylphosphonium bromide and 2.10 g (54 mmol) of sodium amide in 25 ml of toluene was stirred under argon for 24 h and filtered. The solid was washed with toluene. To the orange-coloured filtrate was added 840 mg (5.0 mmol) of *cis*-1 whereupon the mixture turned turbid and acquired an orange-brown colour. The suspension was heated under reflux for 10 h while the conversion was monitored by gas chromatography. The mixture was poured into 200 ml of water. The solid was filtered and washed with pentane. The aqueous layer was extracted with pentane (3 × 25 ml). After drying of the combined extracts with sodium sulfate and distillation of the solvent and the residue at 30 and 16 Torr we obtained 610 mg (74%) of a colourless liquid, b.p. 75°C/16 Torr, d.e. 99% by a comparison of the methyl singlet of *trans*-2 with the carbon-13 satellites of the methyl singlet of *cis*-2 in the proton spectrum. — IR (film):  $\tilde{\nu}$  = 3070 cm<sup>-1</sup> (=CH), 1665 (C=C), 1550 (N=N). — MS: *m/z* (%) = 167 (0.4) [M<sup>+</sup> + 1], 138 (5), 123 (14), 81 (61), 67 (100), 55 (27), 41 (36), 39 (17).

*r*-3,5-Diethyl-3,5-dihydro-*t*-3,5-dimethyl-4-methylene-4H-pyrazole (*trans*-2): The procedure for *cis*-2 described above was followed exactly yielding 560 mg (68%) of a colourless liquid, b.p. 75°C/16 Torr, d.e. 99%. — IR (film):  $\tilde{\nu}$  = 3070 cm<sup>-1</sup> (=CH), 1662

Table 3. Chemical shifts ( $\delta$  values relative to internal tetramethylsilane) in 100-MHz carbon-13 spectra. The chemical shift of carbon atoms equivalent by virtue of symmetry is given only once

Cpd.	$\text{H}_2\text{C}=\text{C}$		$\text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_3$				a)				
<i>cis</i> -2	103.45	156.10	26.12	92.77	32.32	9.08	B				
	103.33	157.24	26.36	92.97	32.78	9.15	C				
<i>trans</i> -2	103.50	154.96	25.03	93.32	33.35	9.05	B				
	103.40	156.08	25.12	93.53	33.83	9.13	C				
<i>cis</i> -8	98.48	153.66	17.84	27.06	27.63	11.87	B				
	98.44	153.67	17.95	26.96	28.02	11.92	C				
<i>trans</i> -8	98.15	154.05	17.24	26.97	28.25	11.61	B				
	98.08	154.04	17.35	26.96	28.62	11.68	C				
(Z)-9 <sup>b)</sup>	14.74	127.14	22.15	22.07	31.09	11.06	20.31	125.08	29.97	13.15	B
	14.86	127.34	22.32	22.44	31.48	11.07	20.11	125.38	30.24	13.22	C
(E)-9 <sup>b)</sup>	16.15	126.73	21.38	20.05	30.91	11.38	20.35	125.54	29.97	12.82	B
	16.23	127.01	21.53	20.47	31.30	11.37	20.29	125.86	30.32	12.86	C
12 <sup>d)</sup>	Cyclopropane Substituents		Isoxazoline Ring				Mesityl Group <sup>e)</sup>				
	$\text{CH}_3$	$\text{CH}_2-\text{CH}_3$	C(1)	C(2)	C(3)	C(6)	C(7)	$\text{CH}_3$	quat.-C	CH	
13	16.37	—	—	22.87	74.90	157.27	37.41	19.70	136.70	128.63	B
	18.36	—	—	23.16	74.95	156.20	37.72	19.85	128.95	128.81	C
<i>cis</i> -14 <sup>f)</sup>	15.05	23.37	11.47	28.29	75.90	156.97	37.99	19.72	136.70	128.85	B
	12.85	25.12	11.35	28.13	75.50	156.84	37.14	19.89	136.75	128.70	C
<i>trans</i> -14	12.55	23.85	11.22	28.26	75.80	156.14	37.65	19.83	128.79	128.75	C
	14.54	26.76	11.37	28.54	—	—	—	21.14	136.89	138.29	

a) Solvent B: [D<sub>6</sub>]benzene, C: [D<sub>12</sub>]cyclohexane. — b) Mixtures of the diastereomers (E)- and (Z)-9. The assignment of the signals to (E)- and (Z)-9 is based on the analysis of mixtures with different ratios of (E)- and (Z)-9. — c) Some signals of the mesityl group could not be identified because of signal overlap. The numbers given in the first place refer to the more intense signal. — d) The signal of the carbon atom of the functional group is missing. It can be detected in the spectrum of the <sup>15</sup>N isotopomer<sup>36)</sup>. — e) Mixtures of *cis*-14A (= major isomer) and *cis*-14B. The numbers given in the first place refer to the more intense signal.

(C=C), 1550 (N=N). — MS: *m/z* (%) = 167 (0.4) [M<sup>+</sup> + 1], 138 (3), 123 (11), 81 (58), 67 (100), 55 (29), 41 (42), 39 (18).

$\text{C}_{10}\text{H}_{18}\text{N}_2$  (166.3) Calcd. C 72.24 H 10.91 N 16.85  
*cis*-2: Found C 72.31 H 11.01 N 16.72  
*trans*-2: Found C 72.47 H 10.86 N 16.59

**Photolysis Experiments:** The NMR sample tubes containing 0.6–0.7 M solutions of *cis*-2 or *trans*-2 were carefully degassed by several freeze-pump-thaw cycles and sealed under a vacuum of 10<sup>-5</sup> Torr. The samples were kept at 20–25°C and irradiated with a 500-W high-pressure mercury lamp (Osram HBO 500 W/2) which was focussed by quartz optics. A 10-cm water filter and a 5-mm cut-off filter, type WG 345 from Schott & Gen., Mainz, were used. The proportions of starting material and products were calculated from integrations of proton signals and peak areas in gas chro-

matograms as well. Specific response factors for the latter were neglected.

**Thermal Isomerization *trans*-8 → (E)- and (Z)-9 and Thermal Equilibration (E)-9 ⇌ (Z)-9:** A [D<sub>6</sub>]benzene solution containing *trans*-8, (E)-9, and (Z)-9 (64:14:22), which was obtained by irradiation of *trans*-2, was heated to 180 ± 0.2°C for 24 h. The proton spectrum and gas chromatogram revealed the presence of equal amounts of (E)-9 and (Z)-9. The solution remained unchanged when heated to 180 ± 0.2°C for 30 d.

**1,1,2,2-Tetramethyl-6-(2,4,6-trimethylphenyl)-4-oxa-5-azaspiro[2.4]hept-5-ene (13):** A mixture of 44 mg (0.4 mmol) of 4, 32 mg (0.2 mmol) of 12, and 0.2 ml of ether was sealed in an evacuated (10<sup>-5</sup> Torr) thick-walled glass tube and heated to 80°C for 24 h. The solvent and the excess of 4 were distilled at 40°C/100 Torr. The oily residue was dried at 50°C/10<sup>-2</sup> Torr crystallized from little pentane at -30°C to afford 44 mg (81%) of colourless crystals, m.p. 53–54°C. — MS: *m/z* (%) = 271 (13) [M<sup>+</sup>], 256 (19) [M<sup>+</sup> - Me], 188 (100), 158 (36), 145 (75), 130 (90), 69 (70).

$\text{C}_{18}\text{H}_{25}\text{NO}$  (271.4) Calcd. C 79.66 H 9.28 N 5.16

Found C 79.39 H 9.12 N 5.15

Exactmass Calcd. 271.1936 Found 271.1937

**Diastereomeric *r*-1,*c*-2-Diethyl-*t*-1,*t*-2-dimethyl-6-(2,4,6-trimethylphenyl)-4-oxa-5-azaspiro[2.4]hept-5-enes (*cis*-14A and *cis*-14B)**

a) A [D<sub>6</sub>]benzene solution of *cis*-8, (E)-9 and (Z)-9 (64:17:19) was obtained by irradiation of *cis*-2. After addition of 32 mg (0.2 mmol) of 12, the mixture was kept at 20–25°C while the reaction was monitored by proton and carbon-13 spectroscopy. Complete conversion of *cis*-8 to a mixture of *cis*-14A and *cis*-14B (63:37) was indicated after 25 d.

b) A [D<sub>12</sub>]cyclohexane solution of *cis*-8, (E)-9, (Z)-9 (64:17:19) and 12 prepared as described under a) was heated to 50°C. The conversion of *cis*-8 to a mixture of *cis*-14A and *cis*-14B (63:37) ran to completion within 2 d.

***r*-1,*t*-2-Diethyl-*t*-1,*c*-2-dimethyl-6-(2,4,6-trimethylphenyl)-4-oxa-5-azaspiro[2.4]hept-5-ene (*trans*-14):** A [D<sub>12</sub>]cyclohexane solution of *trans*-8, (E)-9, (Z)-9 (64:14:22) and 12 prepared from *trans*-2 as described above was heated to 50°C. The conversion of *trans*-8 to *trans*-14 was complete after 2 d.

#### CAS Registry Numbers

*cis*-1: 132540-41-1 / *trans*-1: 132540-42-2 / *cis*-2: 132540-43-3 / *trans*-2: 132540-44-4 / 4: 54376-39-5 / *cis*-7: 132540-45-5 / *trans*-7: 132540-46-6 / *cis*-8: 132540-47-7 / *trans*-8: 132540-48-8 / (E)-9: 132540-49-9 / (Z)-9: 132540-50-2 / 12: 2904-57-6 / 13: 132540-51-3 / *cis*-14A: 132540-52-4 / *cis*-14B: 132618-64-5 / *trans*-14: 132618-65-6 / sodium amide: 7782-92-5 / methyltriphenylphosphonium bromide: 1779-49-3

<sup>1)</sup> Dedicated to Professor Hans Georg von Schnering on the occasion of his 60th birthday.

<sup>2)</sup> Photochemical Formation of Heteromethylenecyclopropanes, 22. — Part 21: H. Quast, H. Jakobi, *Chem. Ber.* **124** (1991) 1613, preceding paper. The results are taken from the *Dissertation* of H. Jakobi, Universität Würzburg, 1991.

<sup>3)</sup> P. Walden, *Ber. Dtsch. Chem. Ges.* **28** (1895) 1287, 2766; **29** (1896) 133; **30** (1897) 2795, 3146; **32** (1899) 1833, 1855.

<sup>4)</sup> R. Huisgen in *1,3-Dipolar Cycloaddition Chemistry* (A. Padwa, Ed.), 1st ed., vol. 1, p. 1, Wiley, New York 1984.

<sup>5)</sup> T. V. Van Auken, K. L. Rinehart, Jr., *J. Am. Chem. Soc.* **84** (1962) 3736.

<sup>6)</sup> P. D. Bartlett, N. A. Porter, *J. Am. Chem. Soc.* **90** (1968) 5317.

<sup>7)</sup> R. S. Givens, *Photoextrusion of Small Molecules in Organic Photochemistry* (A. Padwa, Ed.), 1st ed., vol. 5, p. 227, Marcel Dekker, New York 1981.

- <sup>8)</sup> D. Wendisch in *Methoden der organischen Chemie* (Houben, Weyl, Müller, Eds.), 4th ed., vol. 4/3, p. 42, Thieme, Stuttgart 1971; W. Rundel, *ibid.*, vol. 4/5b, p. 1149 (1975); K. Mackenzie in *The Chemistry of Hydrazo, Azo and Azoxy Groups* (S. Patai, Ed.), 1st ed., p. 374, Wiley, New York 1975; R. J. Drewier, *ibid.*, p. 987; H. Meier, K.-P. Zeller, *Angew. Chem.* **89** (1977) 876; *Angew. Chem. Int. Ed. Engl.* **16** (1977) 835; P. S. Engel, *Chem. Rev.* **80** (1980) 99; W. Adam, O. De Lucchi, *Angew. Chem.* **92** (1980) 815; *Angew. Chem. Int. Ed. Engl.* **19** (1980) 762; R. D. Little, *Chem. Rev.* **86** (1986) 875.
- <sup>9)</sup> M. H. Chang, R. J. Crawford, *Can. J. Chem.* **59** (1981) 2556; R. J. Crawford, M. H. Chang, *Tetrahedron* **38** (1982) 837; G. N. LeFevre, R. J. Crawford, *J. Am. Chem. Soc.* **100** (1986) 1019, and references cited therein.
- <sup>10)</sup> R. J. Bushby, M. V. Jesudason, M. D. Pollard, K. F. Shuhaibar, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2647.
- <sup>11)</sup> R. J. Bushby, M. V. Jesudason, M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2655; R. J. Bushby, *J. Chem. Soc., Perkin Trans. 2*, **1985**, 1211, and references cited therein.
- <sup>12)</sup> W. Adam, M. Dörr, *J. Am. Chem. Soc.* **109** (1987) 1240.
- <sup>13)</sup> Reviews on trimethylenemethane: F. Weiss, *Q. Revs. Chem. Soc.* **24** (1970) 278; P. Dowd, *Acc. Chem. Res.* **5** (1972) 242; J. A. Berson, *ibid.* **11** (1978) 446; in *Rearrangements in Ground and Excited States* (P. De Mayo, Ed.), 1st ed., vol. 1, p. 311, Academic Press, New York 1980; in *Diradicals* (W. T. Borden, Ed.), 1st ed., p. 151, Wiley, New York 1982; W. T. Borden, *ibid.*, p. 24; in *Reactive Intermediates* (M. Jones, Jr., R. A. Moss, Eds.), 1st ed., vol. 2, p. 198, Wiley, New York 1981; *ibid.*, vol. 3, p. 151 (1985); J. J. Gajewski in *Hydrocarbon Thermal Isomerization*, 1st ed., p. 43, Academic Press, New York 1981; B. M. Trost, *Angew. Chem.* **98** (1986) 1; *Angew. Chem. Int. Ed. Engl.* **25** (1986) 1; D. A. Dougherty in *Kinetics and Spectroscopy of Carbenes and Biradicals* (M. S. Platz, Ed.), 1st ed., p. 117, Plenum Press, New York 1990.
- <sup>14)</sup> S. J. Miller, *Adv. Phys. Org. Chem.* **6** (1968) 185; J. Hine, *ibid.* **15** (1978) 1; M. L. Sinnott, *ibid.* **24** (1988) 113.
- <sup>15)</sup> H. Quast, H. Jakobi, B. Seiferling, *Liebigs Ann. Chem.* **1991**, 41.
- <sup>16)</sup> W. L. Mock, *Ph. D. Thesis*, Harvard Univ., Cambridge, Mass., USA, 1964 [*Chem. Abstr.* **65** (1966) 8772c].
- <sup>17)</sup> R. J. Crawford, H. Tokunaga, *Can. J. Chem.* **52** (1974) 4033.
- <sup>18)</sup> H. Quast, H. Jakobi, *Chem. Ber.* **124** (1991) 1613, preceding paper.
- <sup>19)</sup> D. E. Reedich, R. S. Sheridan, *J. Am. Chem. Soc.* **110** (1988) 3697.
- <sup>20)</sup> Addition reactions to the H<sub>2</sub>CC double bond of methylenecyclopropanes have been reported: Epoxidation: J. R. Salaün, J. M. Conia, *Chem. Commun.* **1971**, 1579; D. H. Aue, M. J. Meshishnek, D. F. Shellhamer, *Tetrahedron Lett.* **48** (1973) 4799; J. K. Crandall, W. W. Conover, *J. Org. Chem.* **43** (1978) 3535; J. R. Salaün, J. Champion, J. M. Conia, *Org. Synth., Coll. Vol.* **6** (1988) 320. — [2 + 2] Cycloadditions: M. A. Battiste, *J. Am. Chem. Soc.* **86** (1964) 942; R. Maurin, E. Senft, M. Bertrand, *C. R. Acad. Sci. Ser. C* **269** (1969) 346; W. Hartmann, H.-G. Heine, J. Hinz, D. Wendisch, *Chem. Ber.* **110** (1977) 2986. — Addition of bis(cyclopentadienyl)titanium(III) hydride [from bis(cyclopentadienyl)titanium(IV) dichloride and isopropylmagnesium bromide]: H. Lehmkuhl, S. Fustero, *Liebigs Ann. Chem.* **1980**, 1361. — Addition of electrophilic reagents (bromine, hydrogen bromide, hypobromous acid): B. C. Anderson, *J. Org. Chem.* **27** (1962) 2720; R. Köster, S. Arora, P. Binger, *Liebigs Ann. Chem.* **1973**, 1619. — Oxymercuration: R. M. Babb, P. D. Gardner, *Chem. Commun.* **1968**, 1678. — Oxidation with lead tetraacetate: R. Noyori, Y. Tsuda, H. Takaya, *Chem. Commun.* **1970**, 1181. — Addition of 9-borabicyclo[3.3.1]nonane: A. Maercker, M. Bsata, W. Buchmeier, B. Engelen, *Chem. Ber.* **117** (1984) 2547.
- <sup>21)</sup> D. H. Aue, R. B. Lorens, G. S. Helwig, *Tetrahedron Lett.* **1973**, 4795; *J. Org. Chem.* **44** (1979) 1202; J. K. Crandall, W. W. Conover, J. B. Komin, *ibid.* **40** (1975) 2042.
- <sup>22)</sup> A. Brandi, A. Guarna, A. Goti, F. De Sarlo, *Tetrahedron Lett.* **27** (1986) 1727; A. Brandi, S. Garro, A. Guarna, A. Goti, F. Cordero, F. De Sarlo, *J. Org. Chem.* **53** (1988) 2430.
- <sup>23)</sup> A. Guarna, A. Brandi, A. Goti, F. De Sarlo, *J. Chem. Soc., Chem. Commun.* **1985**, 1518; A. Brandi, A. Guarna, A. Goti, F. De Sarlo, *ibid.* **1986**, 813; A. Brandi, S. Carli, A. Guarna, F. De Sarlo, *Tetrahedron Lett.* **28** (1987) 3845; A. Guarna, A. Brandi, F. De Sarlo, A. Goti, F. Periccioli, *J. Org. Chem.* **53** (1988) 2426; A. Goti, A. Brandi, G. Danza, A. Guarna, D. Donati, F. De Sarlo, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1253.
- <sup>24)</sup> G. Bianchi, R. Gandolfi, P. Grünanger in *The Chemistry of Triple-Bonded Functional Groups* (S. Patai, Z. Rappoport, Eds.), 1st ed., p. 737, Wiley, New York 1983; P. Caramella, P. Grünanger in *1,3-Dipolar Cycloaddition Chemistry* (A. Padwa, Ed.), 1st ed., vol. 1, p. 291, Wiley, New York 1984.
- <sup>25)</sup> C. Grundmann, J. M. Dean, *J. Org. Chem.* **30** (1965) 2809.
- <sup>26)</sup> W. Rahman, H. G. Kuivila, *J. Org. Chem.* **31** (1966) 772; S. Arora, P. Binger, R. Köster, *Synthesis* **1973**, 146; M. Vidal, A. Dussauge, M. Vincens, *Tetrahedron Lett.* **1977**, 313.
- <sup>27)</sup> J.-L. Pierre, M. Vidal, P. Arnaud, C. Gey, *Bull. Soc. Chim. Fr.* **1970**, 1544.
- <sup>28)</sup> H. Quast, W. Rislér, *Angew. Chem.* **85** (1973) 411; *Angew. Chem. Int. Ed. Engl.* **12** (1973) 414; H. Quast, R. Frank, A. Heublein, E. Schmitt, *Liebigs Ann. Chem.* **1980**, 1814.
- <sup>29)</sup> H. Quast, G. Meichsner, *Chem. Ber.* **120** (1987) 1049.
- <sup>30)</sup> M. Barfield, S. Sternhell, *J. Am. Chem. Soc.* **94** (1972) 1905.
- <sup>31)</sup> J. H. Noggle, R. E. Schirmer, *The Nuclear Overhauser Effect*, 1st ed., Academic Press, New York 1971; D. Neuhaus, M. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis*, 1st ed., VCH Verlagsgesellschaft, New York 1989.
- <sup>32)</sup> A. E. Derome, *Modern NMR Techniques for Chemistry Research*, 1st ed., Pergamon Press, Oxford 1987.
- <sup>33)</sup> M. Hesse, H. Meier, B. Zech, *Spektroskopische Methoden in der organischen Chemie*, 3rd ed., Thieme, Stuttgart 1987; H. Günther, *NMR-Spektroskopie*, 2nd ed., Thieme, Stuttgart 1983.
- <sup>34)</sup> P. F. Schatz, RACOON, version 1.2, Univ. of Wisconsin, Madison, Wis., USA, 1983.
- <sup>35)</sup> S. Arora, P. Binger, *Synthesis* **1974**, 801.
- <sup>36)</sup> M. Christl, J. P. Warren, B. L. Hawkins, J. D. Roberts, *J. Am. Chem. Soc.* **95** (1973) 4392.

[6/91]