Retention of Configuration in Two Photochemical Reactions: Formation of Cyclopropanimines by Extrusion of Molecular Nitrogen from Tetraalkyl-4-imino-1-pyrazolines and [2 + 1] Cycloreversion of Cyclopropanimines to Isocyanides and Alkenes[1,2)]

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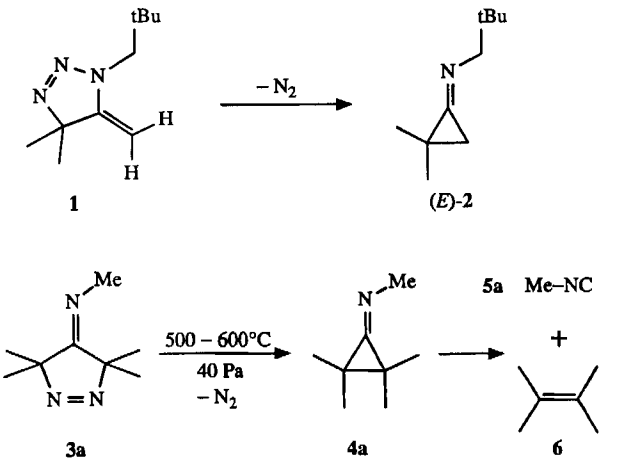
The 1-pyrazolin-4-ones **7** and **9** and the pyrazolidin-4-one **13** are condensed with alkanamines **8** to produce the imines **3**, **10** and **12** in high yields. Direct irradiation of **3** with 350-nm light at 90°C in deuterated hydrocarbon solvents affords the cyclopropanimines **4** in almost quantitative yields besides molecular nitrogen and small amounts of the imines **12** as a result of photoreduction. In [D_6]acetone, the cyclopropanimine **4b** isomerizes in part of the α,β-unsaturated imine **14**. Direct irradiation of **3** with the unfiltered light of the high-pressure mercury lamp results in quantitative [2 + 1] cycloreversion of the primary photoproducts **4** into the alkene **6** and an isocyanide **5**. At low temperature (10°C), photolysis of **3** occurs much more slowly giving rise to photoextrusion of nitrogen (→**4**) and photoreduction (→**12**) to about the same extent. – Photolysis of the stereochemically labelled iminopyrazolines *cis*- and *trans*-**10** (d.e. 99%) at 90°C produces the cyclopropanimines *cis*- and *trans*-**16** (d.e. 94%) with high stereospecificity. The configuration of *cis*- and *trans*-**16** is established by a comparison with the corresponding methylenecyclopropanes *cis*- and *trans*-**19** and the quantitative and completely stereospecific [2 + 1] cycloreversion into methyl isocyanide (**5a**) and the 3,4-dimethyl-3-hexenes (*Z*)- and (*E*)-**17** on irradiation with the unfiltered light of the mercury arc. The necessity of thermal activation for efficient nitrogen extrusion from the $^1(n,\pi^*)$ state of **3** and **10** is indicative of a considerable energy barrier towards the transition into a dissociative state. At low temperature, hydrogen abstraction from the solvent or other molecules becomes important for the deactivation of the $^1(n,\pi^*)$ state, in addition to decay and fluorescence. The stereospecific formation of *cis*- and *trans*-**16** is interpreted in terms of diastereomeric bis-orthogonal azatrimethylenemethane diradicals as intermediates which retain the configuration on cyclization. The minor non-stereospecific path may involve mono-orthogonal azatrimethylenemethane diradicals. Thus, mechanisms that involve the same types of diradical intermediates can rationalize the photolysis of the iminopyrazolines **3**, **10** and of the methylenetriazoline **1** as well. The [2 + 1] cycloreversion of *cis*- and *trans*-**16** into the alkenes (*Z*)- and (*E*)-**17** and methyl isocyanide (**5a**) demonstrates for the first time that such photoreactions can be entirely stereospecific.

The chemistry of cyclopropanones[3)] has been enriched and extented by the syntheses[4–7)] and reactions[8)] of cyclopropanimines. A Favorskii-type 1,3-dehydrobromination of α-bromo ketimines is the method of choice for the synthesis of cyclopropanimines provided that, by virtue of a shielding substitution pattern, they are not too reactive towards nucleophiles[4a)]. On the other hand, highly reactive cyclopropanimines, devoid of ring substituents, are readily available by thermal isomerization of methylenaziridines[4b)]. Eventually, the parent compound has been generated by heterogeneous 1,2-dehydrochlorination of *N*-chlorocyclopropanamine and identified by photoelectron spectroscopy[5)]. We have devised two further approaches which are based on the photochemical[6,7)] or thermal[7)] extrusion of molecular nitrogen from cyclic five-membered azo compounds. While photolysis and thermolysis of the 1,4,4-trialkyl-5-methylene-1,2,3-triazoline **1** occurred very readily to yield stereoselectively the cyclopropanimine **2** in the (*E*) configuration (*E*)-**2**[7)], the thermolysis of the 4-imino-1-pyrazoline **3a** in the photoelectron spectrometer required temperatures exceeding the range of stability of the cyclopropanimine formed (**4a**) which hence decomposed immediately into methyl iso-



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cyanide (**5a**) and 2,3-dimethyl-2-butene (**6**)[9]. We report here on the formation of cyclopropanimines **4** on irradiation of the 4-imino-1-pyrazolines **3** at elevated temperatures. The results have been disclosed partially in a preliminary communication[6]. Furthermore, cyclopropanimines (*cis*- and *trans*-**16**) arise from the *cis*- and *trans*-4-imino-1-pyrazolines *cis*- and *trans*-**10** *with almost complete retention of configuration.* This rules out planar or mono-orthogonal diradicals as intermediates on the main path of product formation and is indicative of bis-orthogonal diradicals (**20**) similar to the bis-orthogonal trimethylenemethanes on the least-motion path leading from 4-methylene-1-pyrazolines to methylenecyclopropanes[10,11].

Synthesis and Spectra of 4-Imino-1-pyrazolines

The 4-imino-1-pyrazolines **3** and **10** were obtained from the pyrazolinones **7** and **9** by condensation with primary amines[12]. Oxidation of the pyrazolidinone **13**[13] to the long-known pyrazolinone **7**[14] has been achieved with manganese dioxide[13], mercuric oxide[15], or chlorine[10]. Crawford's method[13] has now been improved considerably when manganese dioxide on activated carbon[16] was employed instead of conventional grades. The pyrazolinones *cis*- and *trans*-**9** were made available in useful quantities and high diastereomeric purity in a previous study[17].

The condensation of the pyrazolinones **7** and **9** with primary amines **8** was achieved by the method devised by Roelofson and van Bekkum[18] which involves heating of the reactants without solvent in the presence of molecular sieves and an alumina-silica catalyst. The procedure has been employed previously to perform similarly sluggish reactions between encumbered ketones and amines[19,20]. In the present cases, only prolonged heating allowed to overcome the steric hindrance by the ring substituents which was particularly severe in the 3,5-diethyl-3,5-dimethylpyrazolinones *cis*- and *trans*-**9**. Eventually, *cis*- and *trans*-**9** could be forced to condense with methylamine by heating the mixture of ketone and a large excess of the amine for three weeks at temperatures as high as 150°C. Attempts to prepare the imines from *cis*- or *trans*-**9** and neopentylamine (**8b**) met with failure at even higher temperatures because of beginning decomposition. While methyl-, neopentyl-, and cyclohexylamine (**8a–c**) afforded the imines **3a–c** in reasonable yields (Table 1) *tert*-butylamine did not react at all with **7** in the course of several days at 150°C.

The imines **3** and **10** were obtained as colourless liquids or low-melting crystals. The infrared spectra of **3a–c** and *cis*- and *trans*-**10** as well exhibited strong C=N absorptions at 1693–1697 cm^{-1} which appeared by 20 cm^{-1} at higher frequencies than the C=N band of the *N-tert*-butylimine derived from cyclopentanone[19]. An absorption of low intensity around 1540–1545 cm^{-1} was assigned to the NN vibration by comparison with similar tetraalkyl-1-pyrazolines[17].

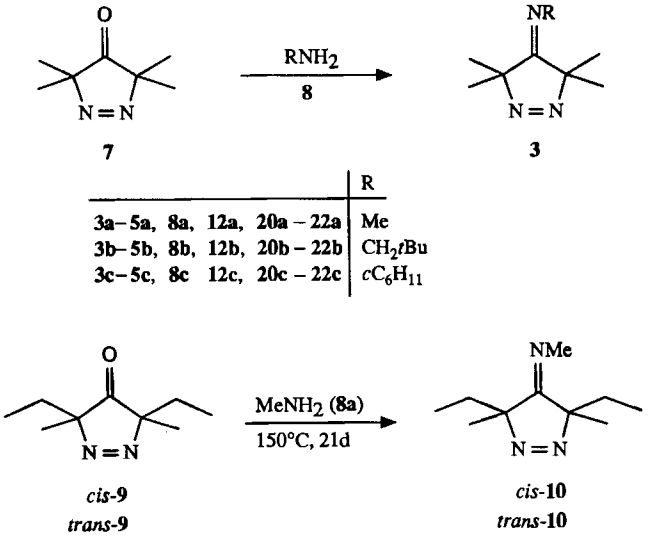
The photoelectron and ultraviolet spectra of **3a** have been interpreted by the aid of semi-empirical calculations. The absorption at the longest wavelength arises from the $(n_-) \rightarrow (\pi^*_{NN})$ transition of the azo group while a band at 273 nm of low intensity has been assigned to the $\pi \rightarrow \pi^*$ transition of the imino group[21]. Thus, the $\pi\pi^*$ absorption occurs at much longer wavelength than that of iminocyclopentanes[22].

The imines **3** and **10** fluoresce. For example, hexane solutions of **3b** exhibit fluorescence devoid of fine structure between 400 and 600 nm with a maximum at 480 nm. The relatively large Stokes shift of more than 100 nm indicates considerably different structures for the thermally equilibrated S_0 and S_1 states. The fluorescence of **3** may be compared to that of **7** which, in hexane solution, exhibits a maximum of very low intensity at 510 nm (quantum yield 0.001)[23].

Table 1. Yields, physical and spectroscopic characteristics of some tetraalkyl-4-imino-1-pyrazolines

Cpd.	Yield [%]	b.p. [°C][a]/Torr (m.p. [°C])	IR [cm^{-1}] (CCl$_4$) C=N	N=N	UV (hexane) λ_{max} (log ε)
3a	53	20–25/10^{-2} (3 - 4)	1696	1545	273 (1.926) 342 (2.308)
3b	85	0/10^{-5} (18.5 - 19)	1697	1546	275 (1.911) 342 (2.308)[b]
3c	70	55/10^{-5} (75 - 75.5)	1693	1545	273 (1.871) 342 (2.282)
cis-**10**	89	20–25/10^{-2}	1697	1538[c]	277 (1.950)[d] 347 (2.274)
trans-**10**	86	20–25/10^{-2}	1694	1538[c]	278 (1.957)[d] 347 (2.283)
12b	49	(61–62)	1692	—	

[a] Bath temperature. The iminopyrazolines **3b** and **c** have been sublimed. — [b] UV (methanol): λ_{max} (lg ε) = 272 nm (1.778), 341 (2.082). — [c] Neat liquid. — [d] Solvent cyclohexane.



The expected shift differences between the nuclei in *syn* and *anti* position relative to the *N*-alkyl group are observed in the proton and carbon-13 spectra (Tables 4 and 5). Thus, the degenerate *syn-anti* isomerization of the imino group is

slow compared to the NMR time scales, as expected[24]. Karabatsos and Lande found that the *syn* β-protons of *N*-alkylketimines experience a larger shift to higher field than the *anti* β-protons when tetrachloromethane is replaced by benzene as solvent[25]. Measurements of this asymmetric solvent-induced shift[26] indicate that the *syn* methyl groups of **3** resonate at lower field than the methyl groups in *anti* position to the *N*-alkyl group.

Decomposition of 4-Imino-1-pyrazolines on Electron Impact

The mass spectra (12 eV) of the imines **3** were scrutinized for similarity between the fragmentation pattern[27] resulting from electron impact and direct excitation of the azo chromophor (see below). The pyrazolinone **7** was included for comparison. In fact, fragmentation of the molecular ions $3^{+\cdot}$ and $7^{+\cdot}$ started with loss of molecular nitrogen. This was proved for $7^{+\cdot}$ by the exact mass of the $M^{+\cdot} - 28$ fragment which is undistinguishable from the $M^{+\cdot} - CO$ fragment in mass spectra of low resolution. Thus, electron impact generates interesting radical cations which may be related to the radical cations of trimethylenemethanes discovered recently[28]. The $M^{+\cdot} - N_2$ radical cations disaggregated further, either by loss of alkyl radicals, viz. methyl or C_3H_7, or cleavage into radical cations derived perhaps from 2,3-dimethyl-2-butene ($6^{+\cdot}$, $C_6H_{12}{}^{+\cdot}$) and isocyanides ($5a^{+\cdot}-5c^{+\cdot}$). A fragment of the latter type did not arise, of course, from $7^{+\cdot} - N_2$ which afforded $C_6H_{12}{}^{+\cdot}$ as the most abundant species.

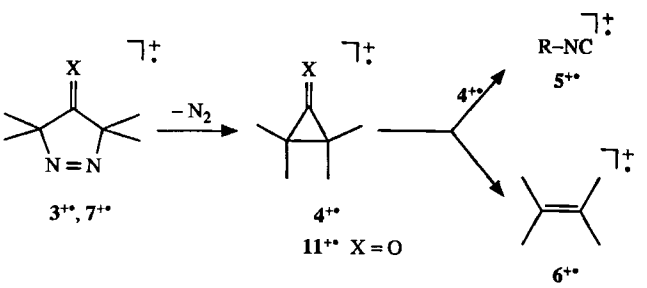
While the nature of the $M^{+\cdot} - N_2$ species can only be speculated about in view of the scarcity of the available evidence, the ion $C_6H_{12}{}^{+\cdot}$ may be rationalized in terms of formation of a carbon–carbon bond in a precursor for which the $M^{+\cdot} - N_2$ fragment is the most likely candidate. Therefore, we tentatively favour the cyclopropane structures $4^{+\cdot}$, $11^{+\cdot}$ over acyclic structures for these species. For the radical cations derived from methylenecyclopropane and trimethylenemethane, however, acyclic structures are calculated to be more stable than the cyclic ones[29].

The fragmentation on electron impact of the 1-pyrazolines **3**, **7** and the corresponding thione[30], the pyrolysis in a photoelectron spectrometer[9], and the decomposition on photolysis as well demonstrate that fundamentally different

Table 2. Relative intensities [%] of the molecular ion and fragment ions in the mass spectra (12 eV) of 4-imino-1-pyrazolines **3** and the pyrazolinone **7**

Cpd.	$M^{+\cdot}$	$M^{+\cdot} - N_2$	$M^{+\cdot} - N_2 - CH_3$	$M^{+\cdot} - N_2 - C_3H_7$	$C_6H_{12}{}^{+\cdot}$ **6**$^{+\cdot}$	$RNC^{+\cdot}$ **5**$^{+\cdot}$
3a[a]	3	2	40	8	71	41
3b	3	11	26	100	93	10
3c	3	5	16	100	43	22
7	16	12[b]	5	34	100	—

[a] Basis peak (100%): $m/z = 56$. — [b] Calculated 112.0888, found 112.0894; calculated for $7^{+\cdot} - CO$: 112.1000.



methods of excitation may furnish similar results. Irrespective of the mode of excitation, similar dissociative states are generated which decompose predominantly into molecular nitrogen in its electronic ground state[31] and a fragment of the (hetero)trimethylenemethane type.

Photolysis of 4-Imino-3,3,5,5-tetramethyl-1-pyrazolines

Carefully degassed solutions of the 4-imino-1-pyrazolines **3** in sealed NMR sample tubes were kept at constant temperatures and irradiated with the filtered (≥345 nm) light of a focussed high-pressure mercury lamp. The samples remained clear and colourless up to high conversions. The course of the photolysis was monitored by proton spectroscopy which was complemented by carbon-13 spectroscopy after termination of the experiment. The results are listed in Table 3.

In hydrocarbon solvents at elevated temperatures, the photolysis of **3** occurred rapidly giving rise to the formation of molecular nitrogen and a single major product in each case. Only small amounts of photoreduction products, e.g. **12** (vide infra), were uncovered by scrutiny of the proton spectra. The cyclopropanimine structure **4** of the predominating photoproducts is based on infrared (**4b**: C=N frequency at 1772 cm^{-1}, cf. ref.[4a]), proton, and carbon-13 spectra (Tables 4 and 5) and the quantitative decomposition into 2,3-dimethyl-2-butene (**6**) and isocyanides **5** when the *unfiltered* light of the high-pressure mercury lamp was employed. The $\pi \rightarrow \pi^*$ excitation of the imine chromophor on irradiation with UV light of short wavelengths induces quantitative [2 + 1] cycloreversion of cyclopropanimines into alkenes and isocyanides. This photocleavage has previously been observed in the case of *N*-(2,2-dimethylcyclopropylidene)neopentylamine[7] and was now confirmed by irradiation of yet another cyclopropanimine having a different substitution pattern, viz. *N*-(2-*tert*-butylcyclopropylidene)-*tert*-butylamine[4a]. Thus, photolysis provides a general and reliable criterion for the presence of a cyclopropanimine structure.

In polar solvents, e.g. [D_6]acetone or [D_6]acetonitrile, at elevated temperatures, the cyclopropanimine **4b** apparently isomerized in part to the α,β-unsaturated ketimine **14**, which was identified by its proton and mass spectrum. An α,β-unsaturated ketimine of this type, e.g. **14** (Ph instead of CH_2tBu), has been obtained instead of the expected cyclopropanone *O*,*N*-acetal when the *N*-phenylimine of tetramethyl-1,3-cyclobutandione was irradiated in methanol solution[32]. The apparent rearrangement of intermediate cyclopropanimines into α,β-unsaturated ketimines in polar

solvents is just another example for an isomerization known to occur in heteromethylenecyclopropanes, e.g. alkylidenethiiranes[9,30], aziridinones[33], aziridinimines[34], and cyclopropanones as well[9]. Most likely, the three-membered ring is cleaved in solution by base catalysis resulting in a ring-opening elimination[35] while unimolecular mechanisms may operate in the gas phase at high temperature and low pressure.

Table 3. Experimental conditions and results of the direct irradiation of the tetraalkyl-4-imino-1-pyrazolines **3** and **10**

Cpd.	[a]	Period of Irradiation [h]	Conversion [%]	Extrusion of N_2 vs. Photoreduction	Products of Extrusion of N_2
	10°C; 345 nm cut-off filter				
3b	B	30	23	54 : 46	**4b**
	C	30	44	63 : 37	**4b**
	90°C; 345 nm cut-off filter				
3a	B	1	65	98 : 2	**4a**
3b	B	1	42	96 : 4	**4b**
	C	1	47	92 : 8	**4b**
3c	B	1	47	[b]	**4c**
cis-**10**	B	0.75	98	98 : 2	*cis*-, *trans*-**16** (97 : 3)
trans-**10**	B	0.75	92	97 : 3	*cis*-, *trans*-**16** (3 : 97)
	90°C; without filter				
cis-**10**	B	0.25	76	99 : 1	[*cis*-, *trans*-**16** (97 : 3)] vs. [(*Z*)-, (*E*)-**17**] = 75 : 25
		0.50	quant.	99 : 1	[*cis*-, *trans*-**16** (97 : 3)] vs. [(*Z*)-, (*E*)-**17** (97.0 : 3.0)[c]] = 42 : 58
trans-**10**	B	0.25	71	99 : 1	[*cis*-, *trans*-**16** (3 : 97)] vs. [(*Z*)-, (*E*)-**17**] = 74 : 26
		0.50	98	98 : 2	[*cis*-, *trans*-**16** (3 : 97)] vs. [(*Z*)-, (*E*)-**17** (2.9 : 97.1)[c]] = 48 : 52

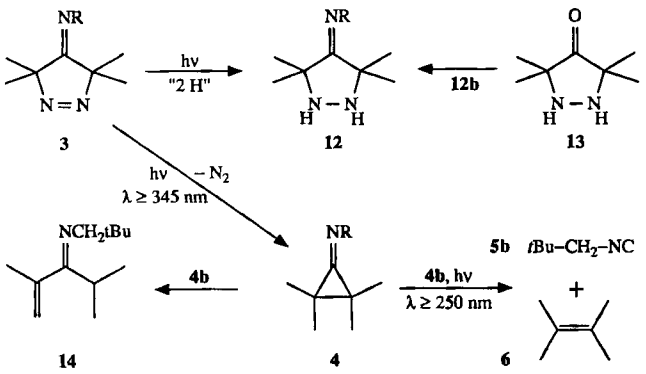
[a] Solvent B: [D_6]benzene, C: [D_{12}]cyclohexane. — [b] The extent of photoreduction could not be determined because of signal overlap in the proton spectrum. — [c] Determined by gas chromatography after extraction with dilute aqueous sulphuric acid. The standard deviation from five gas chromatograms was 0.2%.

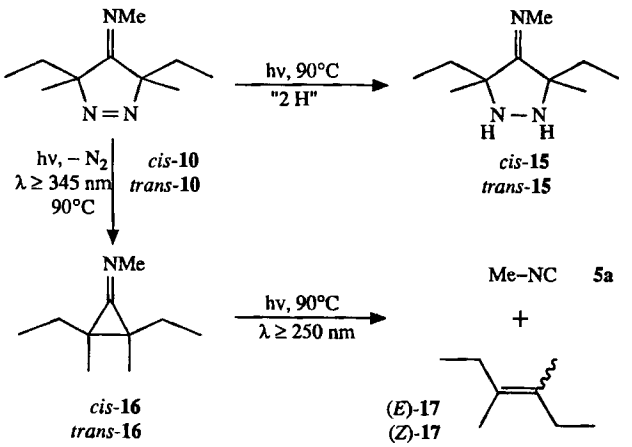
When the imino-1-pyrazoline **3b** was irradiated at 10°C, a second photoproduct became important which was isolated and identified as the 4-iminopyrazolidine **12b** by proton spectroscopy (Table 4) and comparison with an authentic sample obtained by condensation of the pyrazolidinone **13** with neopentylamine (**8b**). The 4-iminopyrazolidine **12b** is formed from **3b** by photoreduction and readily reoxidized by air. The latter property is common to all cyclic hydrazines[36].

Photolysis of *cis*- and *trans*-3,5-Diethyl-3,5-dimethyl-4-imino-1-pyrazolines

The photolysis of stereochemically labelled 4-methylene-1-pyrazolines[11] and 1-pyrazoline-4-thiones[30] derived from the 1-pyrazolinones *cis*- and *trans*-**9** has revealed the steric course of nitrogen extrusion and product formation as well. The results were rationalized in terms of bis-orthogonal trimethylenemethane-type diradicals as primary intermediates which cyclized or isomerized to mono-orthogonal diradicals before ringclosure. The experimental conditions for photochemical cyclopropanimine formation, developed in the preceding section, allowed similar experiments starting from the diastereomeric 4-imino-1-pyrazolines *cis*- and *trans*-**10**. To this end, [D_6]benzene solutions of the latter were kept at 90°C and irradiated through a 345-nm cut-off filter, while the reaction was carefully monitored by proton spectroscopy (400 MHz). Because the photoproducts *cis*- and *trans*-**16** exhibited surprisingly little stability, even in degassed sealed tubes at temperatures as low as −30°C, it was necessary to run the NMR spectra immediately after irradiation and to continue the experiment without delay. With this provision, the total yield of identified products was always higher than 98%. The diastereomeric purity of the substrates *cis*- and *trans*-**10** and photoproducts was estimated by means of carbon-13 satellites of the proton singlets of the major diastereomers. Neither *cis*- and *trans*-**10** nor the photoproducts showed any sign of stereoisomerization during photolysis. The results are listed in Table 3.

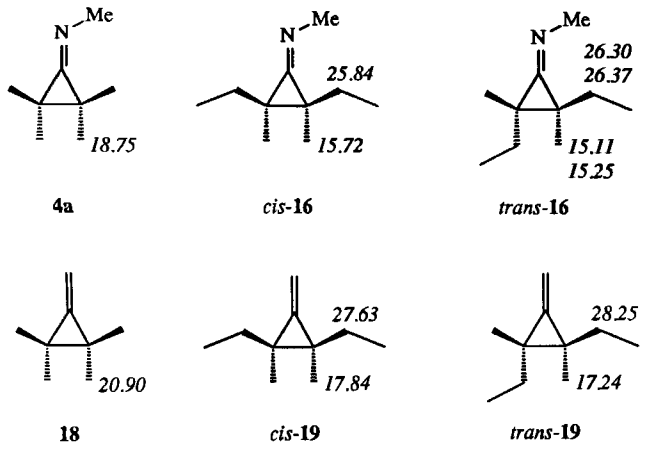
As in the photolysis of the *tetramethyl*iminopyrazolines **3**, the irradiated solutions of *cis*- and *trans*-**10** remained clear and colourless, and only a single major photoproduct was formed in each case besides molecular nitrogen. Obviously, the structure of the predominant product depended on the





configuration of its precursor. Scrutiny of the proton spectra uncovered small amounts of the product from the diastereomeric precursor, however. Thus, given diastereomeric ratios for *cis*- and *trans*-**10** of 99.5:0.5 and 0.5:99.5, respectively, the diastereomeric ratios of 97:3 and 3:97 for the photoproducts revealed a minor non-stereospecific reaction channel. In addition, photoreduction of *cis*- and *trans*-**10** played a detectable, albeit negligible role as could be deduced from the presence of small singlets which are assigned to *cis*- and *trans*-**15** by comparison with the iminopyrazolidine **12a**.

The cyclopropanimine gross structure **16** of the major products was immediately evident from a cursory inspection of the proton and carbon-13 data (Tables 4 and 5) and a comparison with those of the tetramethylcyclopropanimine **4a**. The configurations *cis*- and *trans*-**16** were assigned by a comparison of the carbon-13 spectra with those of the methylenecyclopropanes *cis*- and *trans*-**19** whose configurations have been established unequivocally[11]. The signals of the carbon-13 atoms attached to the ring of *cis*- and *trans*-**19** appear at somewhat higher field when the ethyl group in the neighbourhood stands at the same side of the ring plane. According to this criterion, *cis*-**10** *formed almost only cis*-**16** *and trans*-**10** *almost only trans*-**16**, besides molecular nitrogen and traces of the corresponding 4-iminopyrazolidines **15**. Though proof of the configurations of the compounds **15** has not been attempted, retention of configuration may be assumed for the photoreduction process.



Eventually, the configurations of the cyclopropanimines *cis*- and *trans*-**16** was confirmed by photocleavage to the known stereoisomeric dimethylhexenes (*Z*)- and (*E*)-**17**[37] and methyl isocyanide (**5a**). The stereochemistry of such *photochemical* [2 + 1] cycloreversion reactions of cyclopropane derivatives affording an alkene and a one-carbon fragment has not yet been studied in detail, however[3,38]: *trans*-1,2-di-*tert*-butylcyclopropanone yielded carbon monoxide and *trans*-di-*tert*-butylethylene on irradiation[39], and a 2,4-dimethyl-2,4-dipropylcyclobutane-1,3-dione of unknown configuration was reported to yield an alkene with high stereospecificity in both photodecarbonylations, viz. the first one which produced and the second which destroyed the postulated intermediate cyclopropanone[40].

Despite the obvious scarcity of the pertinent precedent, the photo [2 + 1] cycloreversion of the cyclopropanimines *cis*- and *trans*-**16** seemed suitable to establish a correlation between their configuration and that of the dimethylhexenes (*Z*)- and (*E*)-**17**[37]. To this end, solutions of the iminopyrazolines *cis*- and *trans*-**10** in [D_6]benzene were kept at 90°C and exposed to the *unfiltered* light of the high-pressure mercury lamp. Besides the cyclopropanimines *cis*- and *trans*-**16** as *primary* photoproducts, methyl isocyanide (**5a**) and both alkenes (*Z*)- and (*E*)-**17** were identified as *secondary* photoproducts by high-field proton and carbon-13 spectra (Table 3). The identity of the alkenes was established by comparison with an authentic sample of a 1:3 mixture of (*Z*)- and (*E*)-**17** prepared by the Corey-Winter reaction from the diastereomeric 1,3-dioxolane-2-thiones and triethyl phosphite[37]. In contrast to 60-MHz proton spectra[37], NMR spectra recorded on a high-field spectrometer did exhibit significant, albeit small differences between (*Z*)- and (*E*)-**17** (Tables 4 and 5). Because these shift differences were changed or, for some very close signals, even reversed by the presence of other photoproducts, it was necessary to remove the latter by repeated extraction of the photolysed sample with dilute aqueous sulphuric acid. Thus, the ratio of the diastereomers (*Z*)- and (*E*)-**17** could be estimated from the proton spectra. Eventually, capillary gas chromatography allowed a precise determination. It was gratifying to observe the transformation of *cis*-**10** into (*Z*)-**17** and of *trans*-**10** into (*E*)-**17** with both alkenes exhibiting exactly the same degree of diastereomeric purity which had characterized the intermediate cyclopropanimines *cis*- and *trans*-**16** formed in the first step of the sequence. Thus, photo [2 + 1] cycloreversion of the latter is completely stereospecific.

Discussion

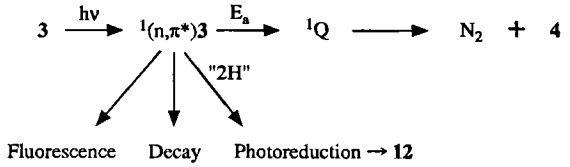
As a result of varying temperature, solvent, and wavelenghts of irradiation, a useful set of experimental parameters for the photochemical synthesis of 2,2,3,3-tetraalkylcyclopropanimines (**4**, **16**) from iminopyrazolines (**3**, **10**) has been developed (Table 3). Cyclopropanimines having such substitution pattern are as yet not available by any other method[4–7].

The products of nitrogen extrusion from iminopyrazolines originate on the least-motion path[41]. Not even traces of methyleneaziridines, e.g. **22**, could be detected which would have resulted on the non-least-motion path. The same observation has already been made when the methylenetriazoline **1** was photolysed producing exclusively the cyclopropanimine (*E*)-**2** but no methyleneaziridine **26**[7]. Therefore, cyclization of any diradical intermediates is determined by product stability.

The rather high temperature (90°C) required for rapid formation and high yields of cyclopropanimines is consistent with an activation energy for the extrusion of molecular nitrogen from the first excited singlet state. Following a suggestion by Turro, Katz and Acton have employed thermal activation of photochemical nitrogen extrusion for the synthesis of prismane as early as in 1973[42]. Cyclic azo com-

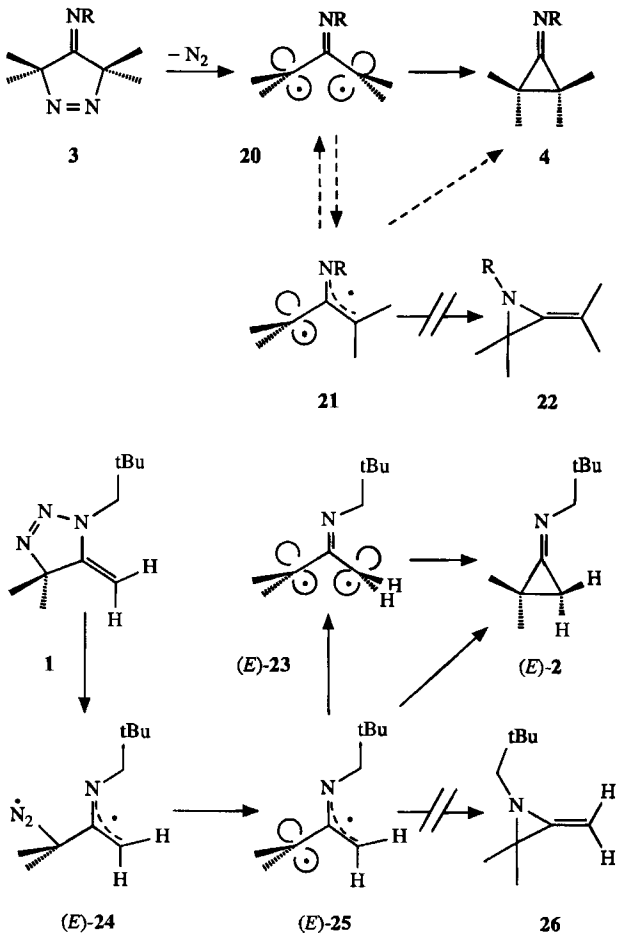
pounds that are unexpectedly reluctant to eliminate nitrogen were shown to be characterized not only by a low quantum yield for photodecomposition but also by a large quantum yield for fluorescence and a long singlet lifetime[23]. Eventually, the barrier to the extrusion of nitrogen from the excited singlet state of 4-isopropylidenetetramethyl-1-pyrazoline was estimated from the temperature dependence of both the fluorescence quantum yield (6.5[43] and 7.9 kcal/mol[44]) and the quantum yield of nitrogen extrusion (10.0 kcal/mol[44]). The fluorescence characteristics have been used as a convenient guide to the selection of the appropriate higher temperature for the photolysis of reluctant *polycyclic* azo compounds[42,45]. The results of the present study demonstrate the usefulness of the fluorescence criterion also for the photolysis conditions of *monocyclic* azo compounds.

Inspection of Table 3 reveals that the temperature not only controls the rate of disappearence of the substrates **3** but that it also strongly influences the ratio of photoreduction versus cyclopropanimine formation. At low temperature, the imines **3** are transformed into photoproducts much more slowly than at 90°C; furthermore, while similar rates for photoextrusion of nitrogen and photoreduction are observed, the latter becomes unimportant at high temperature. Apparently, photoreduction depends only very little, if at all, on the temperature. Photochemical hydrogen abstraction by diethyl azodicarboxylate[46] and azobenzene[47] is well documented. Evidence for photoreduction of 2,3-diazabicyclo[2.2.2]oct-2-ene and derivatives thereof is indirect[23,48,49] except for an early example discovered by Lüttke and Schabacker who isolated and identified the photoreduction product[50]. We have found that photoreduction can be important for 4-substituted 1-pyrazoline derivatives, viz. the pyrazolinone **7**[51], the iminopyrazolines **3** of the present study and 4-methylenepyrazolines as well[11,52]. Therefore, the scheme, devised by Engel and coworkers to accommodate the observations in the photolysis of 2,3-diazabicyclo[2.2.2]oct-2-enes[49], may be complemented as exemplified for **3** in the following scheme: "Direct irradiation populates the $^1(n,\pi^*)$ state, which decays, fluoresces, or decomposes via some dissociative state ^1Q"[49] *or abstracts hydrogen from the solvent or other molecules.* It goes without saying that the latter process is favoured by hydrogen donor solvents, a long lifetime of the singlet state and an energy barrier towards the transition into the dissociative state.



The wavelengths of the light employed for irradiation did not exert an important influence, except that the unfiltered light, being more intense, effected more rapid photolysis and, due to shorter wavelengths, photocleavage of the cyclopropanimines into alkene and isocyanide. As exemplified for *cis*- and *trans*-**10** (Table 3), the cyclopropanimines **16** are formed faster than cleaved. Thus, at complete conversion of the iminopyrazolines **10**, about equal amounts of cyclopropanimines **16**, alkenes **17**, and methyl isocyanide (**5a**) were present.

The results obtained from the photolysis of the stereochemically labelled iminopyrazolines **10** prove that several steps are highly stereospecific, viz. the extrusion of molecular nitrogen after $n \rightarrow \pi^*$ excitation of the azo group, cyclization of any diradical intermediates to yield the cyclopropanimines *cis*- and *trans*-**16**, and eventually the [2 + 1] cycloreversion of the latter into methyl isocyanide (**5a**) and the alkenes **17** after $\pi \rightarrow \pi^*$ excitation of the C=N chromophor. The predominant retention of configuration of the substrates *cis*- and *trans*-**10** in the products *cis*- and *trans*-**16** is not compatible with *mono-orthogonal* azatrimethylenemethanes, e.g. **21**, or any other intermediates that have lost the stereochemical information. Therefore, *bis-orthogonal* azatrimethylenemethanes such as *20* are invoked as most plausible intermediates *on the main route* of the product formation. The discovery of small amounts of cyclopropanimines **16** in the opposite, "wrong" configuration is indicative of an additional stereo-random reaction path, however, which accounts for five percent of the products. In contrast to the main route, the minor non-stereospecific path involves probably mono-orthogonal azatrimethylenemethane intermediates, e.g. **21**. The latter may equilibrate with their bis-orthogonal stereoisomers or cyclize directly



to cyclopropanimines. Thus, the mechanistic picture emerging from the present study can be summarized in the following scheme. For sake of simplicity, it is sketched for *tetramethyl*iminopyrazolines (**3**).

The assumption of diastereomeric azatrimethylenemethanes as intermediates also leads to a mechanistic pictograph for the photolysis of the methylenetriazoline **1** which gives rise to the formation of cyclopropanimine (*E*)-**2**[7]. Rupture of the NN bond that is the shear point of **1** generates the diazenylazaallyl diradical (*E*)-**24**. After loss of molecular nitrogen from (*E*)-**24** affording the mono-orthogonal azatrimethylenemethane diradical (*E*)-**25**, the route merges into that postulated for the non-stereospecific formation of cyclopropanimines **16** from stereochemically labelled iminopyrazolines **10**.

Numerous [2 + 1] cycloelimination reactions of three-membered ring compounds have been studied[3,38]. Retention of configuration is observed in the overwhelming majority of such *thermally activated* reactions. While retention of configuration in the photoextrusion of carbon monoxide from *trans*-2,3-di-*tert*-butylcyclopropanone[39] may well be the result of a *stereoselective* process, the photochemical decomposition of the cyclopropanimine *cis*-**16** into the alkene (*Z*)-**17** and of *trans*-**16** into (*E*)-**17** and methyl isocyanide (**5a**) is the first clear-cut example which uncovered the stereochemical course of a *photo* [2 + 1] cycloelimination: Entirely *stereospecific*.

We thank Mrs. E. Ruckdeschel and Dr. *D. Scheutzow* for recording the high-field NMR spectra, 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

Yields, physical and spectroscopic characteristics: Table 1; MS: Table 2; results of the photolysis experiments: Table 3; ^{1}H NMR: Table 4; ^{13}C NMR: Table 5; elemental analysis: Table 6. – Methods and instrumentation: Ref.[30] – UV: Cary 17 spectrometer of Varian. – Fluorescence spectra: Spectrofluorimeter MPF-44B of Perkin-Elmer, excitation wavelength 300, 330, or 350 nm. – MS: Varian MAT CH7 mass spectrometer connected to an SS 200 data system. The exact mass of the fragment $7^{+\cdot} - N_2$ was determined by means of a Varian MAT SM 1-BH high-resolution mass spectrometer and perfluorokerosine calibration. – Preparative gas chromatography: Varian 920 gas chromatograph. – Gas chromatography: Varian 1400 gas chromatograph, carrier gas N_2, 3- × 0.002-m glass column, filled with Chromosorb W AW/DMCS (80–100 mesh) which was coated with Carbowax 20 M (5%). – Capillary gas chromatography: Packard model 436 chromatograph of Chrompack, equipped with a Shimadzu Chromatopac C-R6A integrator. 50- × 0.0001-m fused silica column coated with 0.12 µm silicon oil CP Sil 5CB; 4.0 bar N_2, split injection 1:50; column temperature C = 60°C, retention times t_R [min] = 17.70 [(*Z*)-**17**], 18.14 [(E)-17], separation factor α = 1.025; 50- × 0.00025-m fused silica column coated with 0.12 µm silicon oil CP Sil 5CB; 1.1 bar H_2, split injection 1:20; C = 80°C, t_R [min] = 18.71 (*trans*-**10**), 18.82 (*cis*-**10**), α = 1.006.

[D_6]Benzene and *[D_{12}]cyclohexane* were dried with $LiAlH_4$, degassed (10^{-5} Torr) and saturated with argon (99.998%). – *Molecular sieves* (3 Å) and *Al_2O_3/SiO_2 crack catalyst* (BASF D10-10) were heated for 6 h at 300–350°C/10^{-3} Torr and kept under N_2. – *Methanamine* (**8a**) was carefully dried with sodium hydroxide pellets and condensed (−20°C) in a calibrated cylinder from which it was evaporated and condensed again in a cooled autoclave (−20°C) under argon. – *Cyclohexanamine* (**8c**) was fractionated through a 1-m column filled with rings of screening wire, b.p. 133–134°C. – *2,2-Dimethylpropanamine* (**8b**)[53], *cis*- and *trans*-**9**[17], *manganese(IV) oxide on activated carbon*[16], and authentic samples of the *isocyanides* **5a**[54] and **5b**[33] were prepared according to known procedures.

(E)- and (Z)-3,4-Dimethyl-3-hexene [(*E*)- and (*Z*)-**17**]

a) *(l)- and (u)-3,4-Dimethyl-3,4-hexanediol:* The procedure described for 2,3-dimethyl-2,3-butanediol was followed[55]. A 3-l three-necked flask, equipped with reflux condenser, dropping funnel, and stainless-steel heavy-duty stirrer (K. K. Juchheim, Laborgeräte und Apparatebau, D-5550 Bernkastel-Kues) was filled with argon (99.998%). A solution of mercuric dichloride (45.0 g, 0.16 mol) in 2-butanone (300 ml, 243 g, 3.37 mol, freshly distilled from calcium chloride) was added dropwise within 15 min to a stirred suspension of magnesium turnings (38.9 g, 1.60 mol) in dry benzene (400 ml, distilled from sodium hydride). After rapid addition (within 10 min) of a mixture of 2-butanone (145 ml, 117 g, 1.63 mol) and benzene (100 ml), the reaction mixture was stirred and heated under reflux on a water bath (85°C) for 12 h. Water (100 ml) was dropped to the very viscous mixture, and heating was continued for 2 h. The yellow solution was decanted through a filter, and the residue was treated with boiling benzene (250 ml) for 15 min. Filtration, distillation of the solvent at normal pressure and the yellow residue in vacuo yielded 179–189 g of a yellow liquid, boiling between 40 and 120°C/17 Torr. Repeated fractionation of the crude product of two runs by means of a 50-cm Spaltrohr column[56] (Fischer, Labor- und Verfahrenstechnik, 5309 Meckenheim bei Bonn) yielded 176 g (24%) of a colourless liquid, b.p. 93–96°C/14 Torr (ref.[57] 37%, b.p. 106–108°C/27 Torr), consisting of equal amounts of both diastereomers; purity ≥99% (GC). Fractionating crystallizations from little ether at −20°C yielded colourless crystals (8.0 g), m.p. 35–40°C, ratio (*l*)/(*u*) diastereomer = 3:1 (^{13}C NMR) [(*l*)-diastereomer: m.p. 52–53°C[57], 52°C[58], 51–52°C[59]; ^{1}H and ^{13}C NMR of both diastereomers: ref.[59]].

b) *(l)- and (u)-4,5-Diethyl-4,5-dimethyl-1,3-dioxolane-2-thione:* Sodium hydride (3.36 g of a 80% suspension in mineral oil, 112 mmol) was heated to 80°C under argon (99.998%) in dry dioxane (50 ml, distilled from sodium). A solution of the diols [8.0 g, 55 mmol, (*l*)/(*u*) = 3:1, prepared in the preceding experiment] in dry dioxane (50 ml) was added dropwise within 15 min. The mixture was heated under reflux for 8 h. Carbon disulfide (4.17 g, 3.3 ml, 55 mmol) was added at ambient temp., and the orange mixture was heated to 70°C for 20 min. Methyl iodide (8.70 g, 3.8 ml, 61 mmol) was added at 20–25°C. The mixture was stirred at 70°C for 30 min, and 1 h without heating. Addition of benzene (300 ml), removal of the solvent in vacuo, distribution of the residue between benzene (120 ml) and dilute aqueous ammonium chloride (150 ml), and extraction of the aqueous phase with benzene yielded a solution which was washed with aqueous potassium hydrogen carbonate and sodium chloride solution and dried with magnesium sulfate. Flash chromatography on a 50- × 4-cm silica gel column with benzene was monitored by IR spectroscopy. The middle fraction yielded 5.06 g (49%) of a pale brown oil. – IR (neat liquid): $\tilde{\nu}$ = 1300 cm^{-1} (vs, C=S), no absorption at 1800 cm^{-1}. – ^{1}H NMR of the (*l*)-diastereomer: ref.[37]

c) The mixture of the (*l*)- and (*u*)-dioxolanethione (5.06 g, 27 mmol, prepared in the preceding experiment) and triethyl phosphite (50 ml) was heated under argon and reflux for 100 h. Within 10 h,

the product was swept by a stream of nitrogen from the hot reaction mixture (170°C) through the reflux condenser into two efficient consecutive cold traps (−78°C) yielding 3.42 g of a colourless liquid. Purification by preparative gas chromatography at 70°C on a 1.5- × 0.006-m glass column filled with Chromosorb P AW/DMCS, which was coated with silicon oil SE 30 (20%) (carrier gas 200 ml/min H_2), and distillation over potassium carbonate afforded 1.13 g (38%) of a colourless liquid, b.p. 118−119°C [(*E*)-**17** b.p. 119.5°C[37]], (*E*)-/(*Z*)-**17** = 3:1 (^{13}C NMR and capillary GC).

3,3,5,5-Tetramethyl-2,3,4,5-tetrahydro-1H-pyrazol-4-one (**13**): A mixture of hydrazine hydrate (150 g, 3.0 mol), ethylenediaminetetraacetic acid (0.4 g), and ethanol (1.0 l) was stirred and heated to 30−40°C. A solution of 2,4-dibromo-2,4-dimethyl-3-pentanone[60] (272 g, 1.0 mol) in ethanol (150 ml) was added dropwise. The mixture was heated under reflux for 3 h and cooled to −20°C for 24 h. The hydrazine hydrobromide was filtered and the solvent distilled at 50°C bath temp./16 Torr. The unreacted hydrazine hydrate was removed by azeotropic distillation with benzene (200 ml). Evaporation of small amounts of solvent, drying of the residue in vacuo, and sublimation at 60−70°C bath temp./10^{-2} Torr yielded a colourlers solid (31%) which contained some 7 formed by air oxidation and may be oxidized to 7 in the next step. Purification of **13** is carried out under nitrogen and is achieved by dissolving the residue in 2 M hydrochloric acid (600 ml) and extraction with ether (4 × 150 ml). Slow addition of sodium hydroxide (90 g, 2.25 mol) at 10−20°C, extraction with dichloromethane (3 × 200 ml), drying of the extracts with potassium carbonate, and distillation of the solvent in vacuo yielded pale pink crystals (100 g, 71%), m.p. 105−115°C. Sublimation at 40°C bath temp./10^{-3} Torr and recrystallization from ether at −20°C afforded colourless crystals, m.p. 122−125°C (115−117°C, 117−117.5[15]).

3,3,5,5-Tetramethyl-3,5-dihydro-4H-pyrazol-4-one (**7**): A suspension of freshly prepared manganese(IV) oxide on activated carbon[16] (130 g) in a solution of **13** (54.0 g, 0.38 mol) in *tert*-butyl methyl ether (1.0 l) was heated under reflux for 30 h while the water, formed in the reaction, was removed by azeotropic distillation through a 40-cm Vigreux column with the help of a cooled water separator (O. Fritz GmbH, 6238 Hofheim a.T.). The mixture was filtered and the black residue treated with boiling *tert*-butyl methyl ether (500 ml) for 5 h in an extractor. Distillation of the solvent at normal pressure yielded colourless needles which were sublimed at 30°C/0.05 Torr on a finger, cooled to −30°C, affording colourless, volatile crystals (49.4 g, 92%), m.p. 87−88°C (ref.[13] 55%, 83.5−85°C). Repeated recrystallizations from petroleum ether (50−70°C) raised the m.p. to 88.5−89°C.

4-(2,2-Dimethylpropylimino)-3,3,5,5-tetramethyl-2,3,4,5-tetrahydro-1H-pyrazole (**12b**): A thick-walled glass tube was filled under argon with **8b**[53] (16.0 g, 183 mmol), **13** (3.56 g, 25 mmol), molecular sieves (3Å, 30 g), and Al_2O_3/SiO_2 catalyst (BASF D10-10, 6 g) and sealed under vacuum. The glass tube was heated to 150°C for 5 d. Under argon, the organic material was transferred into a flask with the help of pentane (500 ml) and the solvent distilled at reduced pressure. Recrystallization of the semicrystalline residue from pentane (20 ml) at −60°C afforded colourless, hygroscopic crystals (2.60 g, 49%), m.p. 61−62°C, which are very rapidly oxidized in the air. − MS (70 eV): *m/z* (%) = 211 (5) [M^+], 196 (1) [M^+ − Me], 155 (8) [$M^+ - C_4H_8$], 141 (35) [$M^+ - C_5H_{10}$], 113 (26), 84 (39), 71 (47), 69 (14), 58 (100), 56 (16).

4-Imino-3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazoles (**3**). *General Procedure:* A 300-ml stainless steel autoclave (C. Roth GmbH, 7500 Karlsruhe) was filled under argon with molecular sieves (3 Å), Al_2O_3/SiO_2 crack catalyst (BASF D10-10), amine **8**, and **7** (14.0 g, 0.1 mol) and heated for 5 d to 110°C (in the case of **3a**) or 150°C (in the preparation of **3b** and **c**). The organic material was dissolved in petroleum ether (30−50°C) and the solution filtered under nitrogen. After distillation of the solvent in vacuo, the residue was distilled (**3a**), sublimed (**3b**), or recrystallized from pentane (**3c**).

3,3,5,5-Tetramethyl-4-(methylimino)-3,5-dihydro-4H-pyrazole (**3a**): Molecular sieves (140 g), catalyst (50 g), **8a** (40 g, 1.28 mol). Distillation afforded a colourless oil (8.14 g, 53%), b.p. 20−25°C bath temp./10^{-2} Torr, which crystallized at −20°C to yield colourless crystals, m.p. 3−4°C.

4-(2,2-Dimethylpropylimino)-3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazole (**3b**): Molecular sieves (120 g), catalyst (21 g), **8b** (64 g, 0.73 mol). Sublimation at 0°C bath temp./10^{-5} Torr on a cold finger (−30°C) yielded colourless crystals (15.0 g, 72%), m.p. 18.5−19°C.

4-(Cyclohexylimino)-3,3,5,5-tetramethyl-3,5-dihydro-4H-pyrazole (**3c**): Molecular sieves (130 g), catalyst (22 g), **8c** (78 g, 0.82

Table 4. Chemical shifts (δ values relative to internal tetramethylsilane) and absolute values of coupling constants [Hz] in high-field proton spectra. The signals are singlets unless specified otherwise

Cpd.	CH_3	(dq) CH_2	CH_3 (t)	^2J[a]	^3J[a]	NR	[b]
3a	1.216,1.357					3.021	B
3b	1.258,1.338					0.938,3.027	B
	1.314, 1.429					0.935, 3.183	C
3c	1.291,1.374					1.10–1.24 1.42–1.57 1.62–1.73 3.24–3.29	B
cis-**10**	1.169,1.302	1.605,1.780 1.933,2.116	0.681 1.041	14.2	7.5	3.013	B
trans-**10**	1.236,1.368	1.594,1.774 1.962,2.091	0.559 0.796	14.2	7.5	3.008	B
4a	1.031,1.074					3.274	B
4b	1.065,1.091					1.069,3.261	B
	1.177, 1.158					0.922, 3.107	C
4c	1.091, 1.102					1.10–1.24 1.42–1.57 1.71–1.85 3.24–3.29	B
cis-**16**[c]	1.036,1.104	1.32–1.60	0.853,0.996	7.4		3.267	B
trans-**16**[c]	1.059,1.122	1.30–1.65	0.848,0.925	7.4		3.267	B
(*E*)-**17**	1.602	2.013 (q)	0.955	7.5			B
(*Z*)-**17**	1.617	2.001 (q)	0.943	7.5			B
12a	1.065,1.180	3.58 (NH, broad)				3.101[d]	B
12b	1.08,1.15	3.62 (NH, broad)				0.98,3.11	B
	1.12,1.24					0.99,3.20	C
cis-**15**[e]						3.119	B
trans-**15**[e]						3.119	B

[a] Average values from the *syn*- and *anti*-ethyl groups. − [b] Solvent **B**: [D_6]benzene, C: [D_{12}]cyclohexane. − [c] The spectra of the ethyl groups could not be analysed completely because of signal overlap. − [d] The data stem from irradiated solutions of **3a** in [D_6]benzene/benzene (4:1). − [e] *cis*- and *trans*-**15** were available only as minor components in mixtures with *cis*- and *trans*-**16**, respectively. Because of extensive overlap, only the signals of the *N*-methyl protons could be identified.

mol). Recrystallization from pentane afforded colourless crystals (15.5 g, 70%), m.p. 75–75.5°C.

r-3,t-5-Diethyl-t-3,c-5-dimethyl-4-(methylimino)-3,5-dihydro-4H-pyrazole (*trans*-**10**): A 150-ml stainless steel autoclave (C. Roth, GmbH, 7500 Karlsruhe) was filled under argon with molecular sieves (3 Å, 29 g), Al_2O_3/SiO_2 crack catalyst (BASF D10-10, 13 g), **8a** (25 ml, 17.5 g, 0.56 mol, at −20°C), and *trans*-**9** (2.30 g, 13.7 mol). The mixture was heated to 150°C for 21 d, while the pressure was 34 bar. After evaporation of the excess of **8a**, the organic material was dissolved in pentane, and the inorganic solids were extracted for 2 d with refluxing pentane (250 ml). Distillation of the solvent at normal pressure and bulb-to-bulb distillation of the residue at 20–25°C bath temp./10^{-2} Torr afforded 2.19 g (86%) of a colourless liquid, d.e. 99% by comparison of the low-field methyl singlet of *cis*-**10** with the carbon-13 satellites of the same singlet of *trans*-**10** ($^1J_{CH}$ = 129 Hz) in the proton spectrum (400 MHz, 0.048 Hz/point). – MS (70 eV): *m/z* (%) = 181 (3) [M^+], 153 (5) [$M^+ - N_2$], 138 (50) [$M^+ - N_2 - Me$], 124 (54) [$M^+ - N_2 - C_2H_5$], 112 (20) [C_8H_{16}], 56 (100).

r-3,c-5-Diethyl-t-3,t-5-dimethyl-4-(methylimino)-3,5-dihydro-4H-pyrazole (*cis*-**10**): The procedure for *trans*-**10** described above was followed yielding (89%) of a colourless liquid, d.e. 99%. – MS (70 eV): *m/z* (%) = 181 (10) [M^+], 153 (5) [$M^+ - N_2$], 138 (49) [$M^+ - N_2 - Me$], 124 (55) [$M^+ - N_2 - C_2H_5$], 112 (24) [C_8H_{16}], 56 (100).

Photolysis Experiments: NMR sample tubes containing 0.6–0.7 M solutions of **3** or **10** were carefully degassed by several freeze-pump thaw cycles and sealed under a vacuum of 10^{-5} Torr. The samples were kept at 10 or 90°C and irradiated with a 500-W high-pressure mercury lamp (Osram HBO 500 W/2), which was focussed by quartz optics, through a 10-cm water filter and a 5-mm cut-off filter, type WG 345 from Schott & Gen., Mainz. The proportions of starting material and products were calculated from integrations of proton signals (400 MHz, 0.048 Hz/point) and, in the case of (*E*)- and (*Z*)-**17**, from peak areas in gas chromatograms as well, after removal of the other components by extraction with 1 M sulphuric acid (2 × 0.2 ml) and drying with potassium carbonate.

4-(2,2-Dimethylpropylimino)-3,3,5,5-tetramethyl-2,3,4,5-tetrahydro-1H-pyrazole (**12b**) *by Photolysis of* **3b**: A degassed solution of **3b** in [D_{12}]cyclohexane, sealed in an NMR sample tube, was irradiated at 5°C, as described above, until quantitative conversion was achieved. The solvent and the very volatile products were removed under argon by distillation at 20–25°C/12 Torr. Sublimation of the residue at 40–60°C bath temp./10^{-3} Torr afforded colourless crystals of **12b** which were identified by comparison with the authentic sample (IR, ^1H NMR).

2,2-Dimethyl-N-[2-methyl-1-(1-methylethyl)-2-propenyliden]-propanamine (**14**): A degassed solution of **3b** (50 µl, 0.24 mmol) and tetramethylsilane (10 µl) in dry [D_6]acetone (500 µL), sealed in an NMR sample tube, was irradiated for 2 h at 90°C as described above. Heating was continued for 3 h yielding 69% of **14** (^1H NMR). Preparative gas chromatography at 120°C on a 3- × 0.01-m column filled with Chromosorb P AW/DMCS, which was coated with silicon oil SE 30 (20%) (carrier gas 180–200 ml/min H_2, retention time 5.5 min), yielded a colourless oil. – MS (70 eV): *m/z* (%) = 181 (5) [M^+], 166 (8) [$M^+ - Me$], 138 (36) [$M^+ - C_3H_7$], 124 (67) [$M^+ - C_4H_9$], 97 (27), 82 (21), 71 (100), 55 (56), 43 (64), 41 (36). – IR (CCl_4): $\tilde{\nu}$ = 1658 cm^{-1} (C=N), 1632 (C=C). – ^1H NMR ([D_6]acetone): δ = 0.90 (*t*Bu), 1.08 (d, *J* = 6.6 Hz, 2 Me), 1.78 (mc, Me), 2.54 (mc, CH), 3.00 (mc, CH_2), 4.67, 5.09 (2 mc, $=CH_2$).

Table 5. Chemical shifts (δ values relative to internal tetramethylsilane) in high-field carbon-13 spectra. The chemical shift of carbon atoms equivalent by virtue of symmetry is given only once

Cpd.	CH_3	CH_2—CH_3		NR	C(3),C(5)	C=N	[a]
3a	22.50 25.63			39.69	82.26 88.03	179.71	B
3b	23.01 25.66			63.58,32.33 27.75	82.15 88.10	178.01	B
	23.37 25.89			64.35,32.82 28.01	82.37 88.48	178.77	C
3c	23.91 25.79			61.18,34.22 25.97,24.46	82.27 87.81	175.96	B
cis-**10**	21.74 24.17	29.24 30.75	9.01 9.71	39.40	86.98 90.77	178.75	B
trans-**10**	20.69 22.60	29.42 32.61	9.19 9.71	39.40	87.43 91.68	178.02	B
					C(2),C(3)		
4a[b]	18.75			44.36	21.92 22.77	179.99	B
4b	18.86 19.02			70.33,32.25 28.09	21.72 22.26	178.85	B
	19.06 19.40			70.67,32.57 28.23	22.04 22.57	177.97	C
4c	18.94 19.51			66.25,35.03 26.20,25.11	21.85 22.11	176.51	B
cis-**16**[b]	15.72	25.84	11.62 11.89	44.74	27.74 27.95	180.03	B
trans-**16**	15.11 15.25	26.30 26.37	11.29 11.37	44.61	27.83 28.04	180.27	B
						C=C	
(*E*)-**17**	18.01	27.36	13.53			129.30	B
(*Z*)-**17**	17.38	27.90	12.83			129.24	B

[a] Solvent B: [D_6]benzene, C: [D_{12}]cyclohexane. – [b] The *syn* and *anti* carbon atoms attached to the cyclopropane ring resonate at the same frequency.

Table 6. Formula, mass and elemental analysis of the 4-imino-1-pyrazolines **3** and **10**, and of the 4-imino-pyrazolidine **12b**

Cpd.	Formula	Mass		Elemental Analysis		
				C	H	N
3a	$C_8H_{15}N_3$	153.2	Calcd.	62.71	9.87	27.42
			Found	63.50	10.07	27.97
3b	$C_{12}H_{23}N_3$	209.3	Calcd.	68.85	11.07	20.07
			Found	69.30	11.17	20.53
3c	$C_{13}H_{23}N_3$	221.3	Calcd.	70.54	10.47	18.98
			Found	70.29	10.39	19.00
cis-**10**	$C_{10}H_{19}N_3$	181.3	Calcd.	66.26	10.56	23.18
			Found	66.16	10.77	23.20
trans-**10**			Found	66.15	11.14	22.72
12b	$C_{12}H_{25}N_3$	211.4	Calcd.	68.19	11.92	19.88
			Found	67.39	11.93	20.42

CAS Registry Numbers

3a: 72443-11-9 / **3b**: 72443-12-0 / **3c**: 72453-29-3 / **4a**: 72443-13-1 / **4b**: 72443-14-2 / **4c**: 134881-83-7 / **7**: 30467-62-0 / **8a**: 74-89-5 /

8b: 5813-64-9 / **8c**: 108-91-8 / *trans*-**2**: 74097-35-1 / *trans*-**10**: 134881-81-5 / *cis*-**10**: 134881-82-6 / **12a**: 72443-16-4 / **12b**: 72443-17-5 / **13**: 55790-79-9 / **14**: 134881-86-0 / *cis*-**16**: 134881-84-8 / *trans*-**16**: 134881-85-9 / (*E*)-**17**: 19550-88-0 / (*Z*)-**17**: 19550-87-9 / 2-butanone: 78-93-3 / (*l*)-3,4-dimethyl-3,4-hexanediol: 134881-78-0 / (*u*)-3,4-dimethyl-3,4-hexanediol: 32388-93-5 / (*l*)-4,5-diethyl-4,5-dimethyl-1,3-dioxolane-2-thione: 134881-79-1 / (*u*)-4,5-diethyl-4,5-dimethyl-1,3-dioxolane-2-thione: 134881-80-4 / 2,4-dibromo-2,4-dimethyl-3-pentanone: 17346-16-6

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[1] Dedicated to Professor *Karl Heinz Büchel* on the occasion of his 60th birthday.

[2] Photochemical Formation of Heteromethylenecyclopropanes, 24. – Part 23: Ref.[30]. The results are taken from the *Dissertations* of A. Heublein (1976), A. Fuß (1981), B. Seiferling (1984), and H. Jakobi (1991), Universität Würzburg.

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