Photoreduction on Irradiation of 3,3,5,5-Tetramethyl-4-methylene-1-pyrazoline. – An Overlooked Example of a Reaction Competing with the Extrusion of Molecular Nitrogen from Reluctant Azoalkanes[1]

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Received January 2, 1991

Key Words: 4*H*-Pyrazoles, 3,5-dihydro-3,3,5,5-tetramethyl- / 1-Pyrazoline, 4-methylene- / 1*H*-Pyrazole, 2,3,4,5-tetrahydro-3,3,5,5-tetramethyl-4-methylene- / Photolysis / Photoreduction / Extrusion of molecular nitrogen

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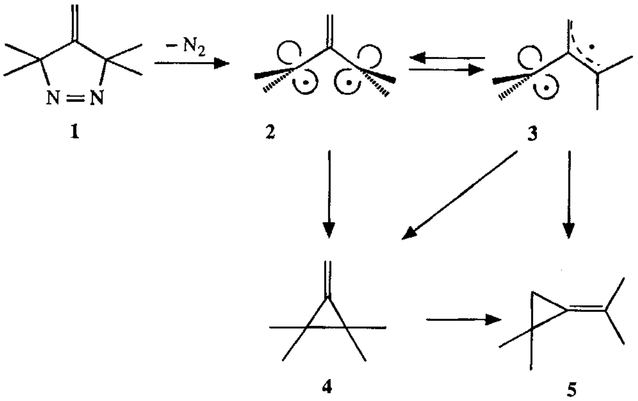
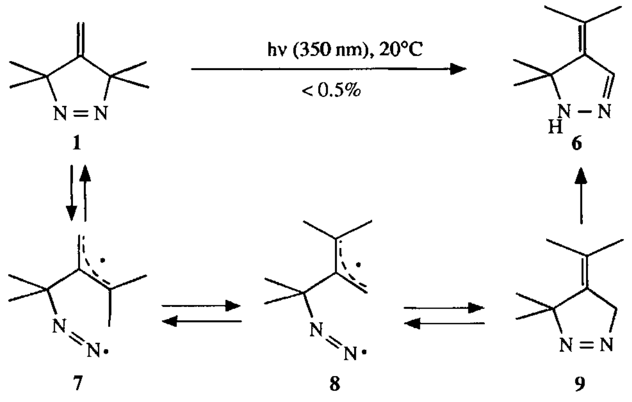
The photolysis of the 4-methylene-1-pyrazoline **1** is reinvestigated under a variety of experimental conditions. Direct irradiation (350-nm light) affords the alkylidenecyclopropanes **4** and **5** as predominant products, besides molecular nitrogen, and in a constant ratio of $(55 \pm 1):(45 \mp 1)$, which is not altered in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) or piperylene nor in $[D_6]$acetone solution. When oxygen is excluded, an additional compound is formed whose proportion depends on the capability of the solvent to act as hydrogen donor. In the presence of three equivalents of DABCO, it eventually becomes the major product. The 4-methylenepyrazolidine structure **13** of the novel photoproduct is established by NMR spectroscopy, a comparison with an authentic sample, obtained in quantitative yield by zinc reduction of **1**, and reoxidation to **1** as well. An extensive investigation to detect any traces of the 4-isopropylidene-2-pyrazoline **6** in the irradiated solutions has failed. This result is at variance with recent disclosures reporting evidence for a turnaround photoisomerization of **1** via diazenylallyl diradicals. The contribution of photoreduction to the decay of the first excited singlet state of reluctant azo compounds is emphasized.

Numerous investigations have been concerned with the mechanism and applications of the photoextrusion of molecular nitrogen from 4-alkylidene-1-pyrazolines[2,3]. Irradiation of such azo compounds represents a convenient route to alkylidenecyclopropanes and to matrix-isolated trimethylenemethanes as well[4], which have been invoked as intermediates in solution and gas-phase photolysis. Following the pioneering work of Andrews and Day[5], Bushby and coworkers[6] have studied the regioselectivity of alkylidenecyclopropane formation in the direct photolysis of 4-alkylidene-3,3,5,5-tetramethyl-1-pyrazolines, i.e. the ratio of the least-motion products vs. the thermodynamically favoured non-least-motion products[7], e.g. **1** → **4**, **5**[6,8]. The observed increase in regioselectivity with the number and bulkiness of substituents at the double bond has been rationalized by *simple* working hypotheses among other possible more elaborate ones. The favoured explanation involved the initial formation of bis-orthogonal trimethylenemethanes, e.g. **2**, which may cyclize to the least-motion product, e.g. **4**, or equilibrate to a greater or lesser extent – depending on the bulkiness of the substituents – with mono-orthogonal trimethylenemethanes, e.g. **3**, assumed as precursors for both isomeric alkylidenecyclopropanes, viz. **4** and **5**[6]. In fact, this hypothesis could be supported later by estimates of the influence of methyl substituents on trimethylenemethane diradicals in the planar and mono-orthogonal geometries[9].

More recently, Adam and Dörr have detected traces (ca. 0.5%) of a third product in the direct photolysis of **1** in pentane solution. The trace component is identified as the 2-pyrazoline **6** by combinations of capillary gas chromatography with mass spectrometry and of gas chromatography with Fourier-transform infrared spectroscopy as well as by a comparison of retention times on several capillary gas chromatography columns. 1,3-Dipolar cycloaddition of tetramethylallene and diazomethane to afford **9** followed by tautomerization provided an authentic sample of **6** which is characterized by analytical and spectroscopic techniques. The implied photoisomerization **1** → **9** is rationalized in terms of the intermediate diazenylallyl diradicals **7** and **8** which in turn lend credibility to theoretical arguments[10].



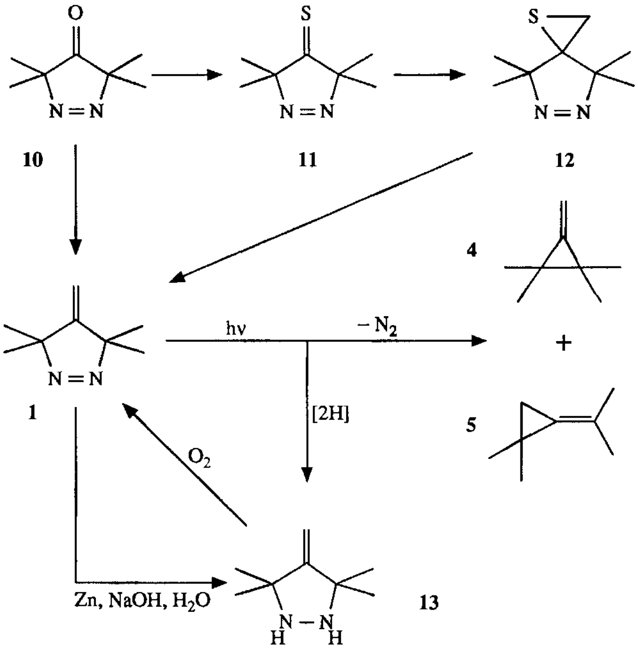
The discovery of **6** and hence the implication of the turnaround photoisomer **9** have met with scepticism[11], however, because a similar *bicyclic* azo compound, namely Berson's 7-isopropylidene-2,3-diazabicyclo[2.2.1]hept-2-ene, isomerizes in this way only *thermally* but *not photochemically*[12] and, in particular, none of the *monocyclic* 4-alkylidene-1-pyrazolines investigated until now isomerizes at all, neither on photolysis[6,8] nor on thermolysis[13]. Surprisingly, there is also a striking disagreement as to the ratios of least-motion product **4** versus non-least-motion product **5** reported in the more recent[10] and in previous studies[6,8] (see below). In view of our interest in the photolysis of the 1-pyrazolin-4-one **10** and -thione **11**[14] and imines derived thereof[15], all closely related to **1**, and in order to set the stage for the first study of *cis/trans*-isomeric 3,3,5,5-tetraalkyl-4-methylene-1-pyrazolines as well[16] we have, therefore, reinvestigated the photolysis of **1**. While we have been unable to confirm the photochemical formation of the tautomer **6** of the alleged turn-around photoisomer **9**[10] we have found variable amounts of a photoreduction product (**13**) which, apparently, has escaped detection so far.



The methylenepyrazoline **1** has been synthesized from ketone **10** by a Wittig reaction in dimethyl sulfoxide with sodium hydride as the base[8,17] or in a three-step sequence via the thione **11** and the spirocyclic thiirane **12**[18]. We have used the Wittig reaction of **10** employing sodium amide in ether for the generation of the ylide[19] and obtained **1** as low-melting crystals of very high purity (≥ 99.9% by capillary gas chromatography). Traces of unreacted ketone **10** – if there are any – are readily removed from the organic phase by extraction with an aqueous solution of $NaBH_4$.

The methylenepyrazoline **1** as well as its photoproducts, i.e. the alkylidenecyclopropanes **4** and **5**, are characterized by high-field proton (Table 2) and carbon-13 spectra (Table 3) run in [D_6]benzene and [D_{12}]cyclohexane which are also used in most of the photolysis experiments. The spectra are in agreement with those recorded in other solvents[17,20]. Moreover, it has now been possible to resolve all of the expected longe-range couplings in the proton spectrum of the isopropylidenecyclopropane **5**, i.e. the coupling $|{}^4J|$ = 0.4 Hz[21] within the isopropylidene group besides its *cisoid* ($|{}^5J|$ = 1.5 Hz) and *transoid* ($|{}^5J|$ = 1.8 Hz) homoallylic coupling with the ring protons. The assignment of the latter coupling constants is based on the useful rule that for homoallylic couplings $^5J_{cisoid}$ is smaller than $^5J_{transoid}$[22]. This has proven true for **5** by nuclear Overhauser enhancement experiments[23]. Irradiation with the resonance frequency of the ring methyl protons increased the signal of the methyl group on the same side of the double bond by 3%, while saturation of the methyl protons on the other side intensifies the signal of the ring protons by 2%. Barfield and Sternhell have considered that the apparently equal *cisoid* and *transoid* homoallylic coupling constants in some ethylidenecyclopropanes may constitute genuine exceptions, which may be related to the unusual bonding associated with three-membered rings[22]. The present results demonstrate that this does not apply, at least not to the isopropylidenecyclopropane **5**. In fact, the reported equality between $^5J_{cisoid}$ and $^5J_{transoid}$ for similar alkylidenecyclopropanes may well be an artefact caused by insufficient resolution and signal separation in low-field proton spectra[24].

Extrusion of nitrogen from the molecular ion of **1** with concomitant formation of an interesting trimethylenemethane radical cation is the major path of fragmentation, as revealed by the 70-eV mass spectrum. The parent trimethylenemethane radical cation is calculated to be more stable than the methylenecyclopropane radical cation[25]. Aryl-substituted trimethylenemethane radical cations have been generated by photosensitized electron transfer from the corresponding methylenecyclopropanes[26].



Methods

For the photolysis experiments, 0.6–0.7 molar solutions of **1** contained in NMR tubes were used which were either flushed with dry nitrogen or oxygen or carefully degassed by several freeze-pump-thaw cycles and sealed under high vacuum. One experiment was carried out in aerated pentane as solvent. The samples were kept at 20–25°C and irradiated with a focussed high-pressure mercury lamp through a 345-nm cut-off filter. A 295-nm cut-off filter was employed in an experiment carried out in [D_6]acetone. The course of the photolyses was monitored by NMR spectroscopy (400 MHz) and, after termination of the irradiation, by gas chromatography on a very efficient column which yielded base-line separation of the isomeric alkylidenecyclopropanes **4** and **5**. The amounts of trace components were estimated from singlets in proton spectra by a comparison with the carbon-13 satellites of the singlets of the major products. Thus, this method of analysis reached similar limits of detection as gas chromatography. The experimental conditions and results are compiled in Table 1.

Table 1. Effects of experimental conditions and the additives 1,4-diazabicyclo[2.2.2]octane (DABCO) and piperylene on the product ratios obtained by irradiation of the methylenepyrazoline **1** through a 345-nm cut-off filter

Solvent	Period of Irradiation [h]	Conversion [%]	**(4 + 5) : 13** = Extrusion of N_2 vs. Photoreduction[a)]	**4 : 5**	Method of Analysis
Pentane	25	85	> 99.9 : < 0.1	55 : 45	GC
Pentane (under O_2)	25	97 96	> 99.9 : < 0.1 > 99.9 : < 0.1	54 : 46 56 : 44	NMR GC
Pentane (degassed)	25	86 85	87 : 13 (97 : 3)	54 : 46 56 : 44	NMR GC
[D_{12}]Cyclohexane (under N_2)	25	83 83	95 : 5 (97 : 3)	53 : 47 55 : 45	NMR GC
[D_{12}]Cyclohexane (under N_2, + 0.45 equiv. DABCO)	25	40 39	63 : 37 (81 : 19)	54 : 46 53 : 47	NMR GC
[D_{12}]Cyclohexane (degassed, + 3 equiv. DABCO)	25	35 34	45 : 55 (57 : 43)	51 : 49 50 : 50	NMR GC
[D_6]Benzene (degassed)	9	98 98	> 99 : < 1 > 99.9 : < 0.1	54 : 46 55 : 45	NMR GC
[D_6]Benzene (under N_2, + 7 equiv. piperylene)	9	17	> 99.9 : < 0.1	54 : 46	GC
[D_6]Acetone[b)] (under N_2)	0.33	97	> 99.9 : < 0.1	53 : 47	GC
[D_6]Acetone (under N_2)	2	48	> 99.9 : < 0.1	54 : 46	GC

[a)] The ratios given in brackets are regarded as less reliable, because the photoreduction product **13** exhibited peak tailing in the gas chromatograms which was detrimental to the precision of the electronic integrations. Furthermore, the ratios were calculated with neglect of specific response factors. — [b)] A 295-nm cut-off filter was used.

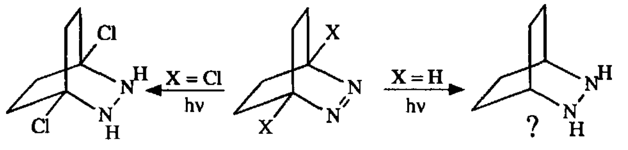
Results

The known alkylidenecyclopropanes **4** and **5** were formed as predominant products in all experiments and readily identified by proton and carbon-13 spectra. The ratios of least-motion product **4** versus non-least-motion product **5** remained unchanged during the course of all photolyses and clustered round the value of $(55 \pm 1):(45 \mp 1)$. This agreed well with the proportions reported by Crawford and Tokunaga (**4**:**5** = 57:43 at 0°C in pentane solution, Pyrex filter)[8)], and Bushby et al. (**4**:**5** = 52:48 at 20–25°C in benzene solution, Pyrex filter)[6)], but was at variance, however, with the ratio found by Adam and Dörr (**4**:**5** = 75:25 at 20°C in pentane solution under nitrogen, 350-nm irradiation)[10)].

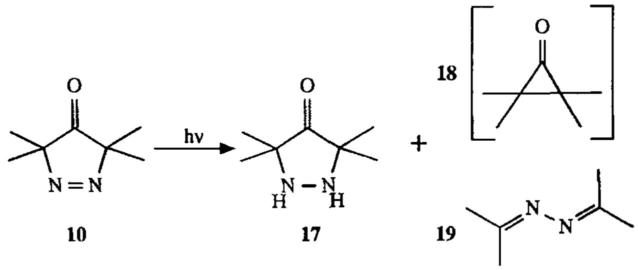
While we were unable to detect any trace of a third photoproduct when **1** was irradiated in aerated pentane solution or in pentane under oxygen, using carefully degassed samples in the same solvent, we observed indeed as much as 13% of a third photoproduct. This was considerably more than could be expected on the basis of the recent disclosure[10)]. The photoproduct formed *in the absence of oxygen* had longer retention times in the gas chromatography than the alkylidenecyclopropanes **4**, **5** and the methylenepyrazoline **1** as well, and exhibited a characteristic peak tailing. The amount of the third photoproduct allowed the direct recording of proton and carbon-13 spectra after termination of the irradiation. To this end, we replaced pentane by [D_{12}]cyclohexane. The NMR spectra recorded from the irradiated solutions *immediately excluded the reported tautomer* **6**[10)] *of the hypothetical turnaround photoisomer* **9** *as a possible structure.* The numbers of signals, viz. two in the proton spectrum (a third, broad signal shown by the spectrum of the pure compound was hidden by the noise), four in the carbon-13 spectrum, suggested a structure of C_{2v} symmetry as in the case of the precursor **1**. That the novel photoproduct had indeed the same set of carbon-bound protons and the same carbon skeleton as **1** was demonstrated by the positions and the multiplicities of the signals in proton and off-resonance decoupled carbon-13 spectra. Most significantly, the signal of quaternary carbon atoms, assigned to ring carbon atoms next to nitrogen, appeared at much higher field (δ = 65.3) than the corresponding signal of **1** (δ = 89.7) (Tables 2 and 3). Thus, the NMR evidence pointed to structure **13** for the third photoproduct. This assumption was readily proven to be true by a comparison with an authentic sample. Reduction of **1** by zinc dust in aqueous sodium hydroxide[27)] afforded colourless crystals melting at 75–76°C in quantitative yield. The structure **13** of the zinc reduction product was confirmed by analytical and spectroscopic methods. In particular, a broad singlet around δ = 3.4, assigned to the equivalent protons bound to nitrogen, was uncovered in the proton spectrum of the pure compound. The mass spectrum revealed the loss of a methyl group from the molecular ion (m/z = 140) but not the elimination of molecular nitrogen. The identity of the authentic **13** and the novel photoproduct was established beyond doubt by a comparison of the NMR spectra and the retention times in the gas chromatography.

The 4-methylenepyrazolidine **13** is sensitive towards molecular oxygen by which it is readily reoxidized to the methylenepyrazoline **1**, particularly in solution. This reaction offers a simple explanation for the observation that the proportion of **13** among the photoproducts formed in saturated hydrocarbons depends on the extent to which molecular oxygen has been excluded. Another factor, influencing the observed ratios of photoreduction of **1** vs. photoextrusion of nitrogen from **1**, appears to be the strength of the carbon-hydrogen and carbon-deuterium bonds present in the solvent molecules. This is indicated by the formation of only traces or the complete lack of **13** when the photolyses are carried out in [D_6]benzene or [D_6]acetone solutions. On the other hand, addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) which is known not only as a singlet quencher[28,29)] but also as a photochemical reducing agent as well[28,30)] dramatically increases the proportion of the photoreduction product **13**. Eventually, **13** becomes the major product in the presence of three equivalents of DABCO.

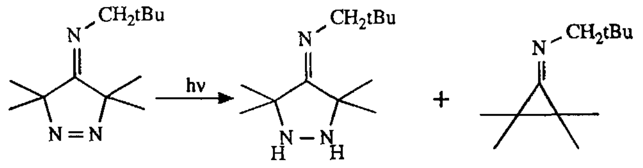
Only a few experiments have been carried out to probe the participation of triplet species in the photochemical events. Neither the presence of seven equivalents of the triplet quencher piperylene nor the use of the possible triplet sensitizer [D$_6$]acetone as solvent affects the ratio of least-motion versus non-least-motion product (**4**:**5**).



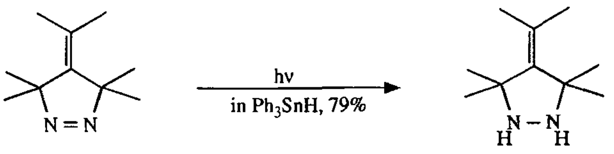
14 **15** **16**



10 **17** **18** **19**



20 **21** **22**



23 **24**

Discussion

The direct irradiation of the methylenepyrazoline **1** in saturated hydrocarbons in the *absence of molecular oxygen* affords the photoreduction product **13** besides the alkylidenecyclopropanes **4** and **5** which arise in a constant ratio of (55 ± 1) : (45 ∓ 1). Photoreduction of cyclic azo compounds by the solvent, acting as predominant source of the hydrogen atoms, is by no means a novel reaction. On direct irradiation of the dichlorodiazabicyclooctene **15** (X = Cl) in hexane or ether, Lüttke and Schabacker have obtained the bicyclic hydrazine derivative **14** and ammonium chloride. Only hydrogen-free solvents allow the detection of nitrogen extrusion products[31]. Steel and coworker have studied the direct photolysis of the parent diazabicyclooctene **15** (X = H). Besides molecular nitrogen and C$_6$ hydrocarbons, they have observed formation of a singlet quencher, assumed to be **16**, from the excited singlet state of **15**[32].

The direct irradiation of the tetramethyl-1-pyrazoline derivatives **10** and **20** affords the photoreduction products **17**[14] and **21**[15] in proportions depending on the experimental conditions. The major photoproducts, viz. **18** + **19** and **22**, arise by extrusion of stable fragments from the pyrazoline ring[14,15]. An attempt to trap a presumed trimethylenemethane intermediate with a good hydrogen source, by irradiating the isopropylidenepyrazoline **23** in triphenyltin hydride, results in the isolation of the photoreduction product **24** in high yield[6].

A common feature of cyclic azo compounds that form photoreduction products is an activation barrier to the extrusion of molecular nitrogen from the excited singlet state[33]. The bicyclo[2.2.2]octanes **15** are well-known prototypes of reluctant azoalkanes[2]. In particular, an activation energy of 6–10 kcal/mol has been determined for the isopropylidenepyrazoline **23**[33], and the photolysis of the pyrazolinimine **20** could be significantly accelerated by employing elevated temperatures[15]. The methylenepyrazoline **1** survives irradiation for seven hours in [D$_8$]toluene solution at −55°C without any noticeable decomposition, thus corroborating the existence of an activation barrier towards nitrogen extrusion. As can be deduced from these examples, photoreduction may well be an hitherto overlooked reaction channel for the deactivation of the excited singlet state of other reluctant azoalkanes. While in the meantime direct evidence has been provided for a photochemical turnaround isomerization via diazenylallyl diradicals of a pair of *polycyclic* azo compounds[11], the enigma of this rearrangement in the alkylidene-1-pyrazoline series[10] remains to be solved.

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. Scheutzow* 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; ^{1}H NMR: Table 2; ^{13}C NMR: Table 3. — Melting points: Sealed capillary tubes, Büchi apparatus. — NMR: Bruker WM 400, 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[34]. In order to achieve resolution of signals very close together and of small long-range couplings, we carried out a Lorentzian-to-Gaussian line-shape transformation[34]. Proton spectra of higher order were analysed by standard methods[35] and simulated with the help of the program RACOON[36]. The assignment of carbon-13 signals was confirmed by DEPT spectra[34]. The sample tubes used in the NOE experiments were carefully degassed by several freeze-pump-thaw cycles and sealed under high vacuum (10^{-5} 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. – A Varian 1400 gas chromatograph equipped with a Shimadzu Chromatopac C-R6A integrator was applied to GLC analyses on 3 × 0.002 m glass columns packed with 10% silicon oil SE 30 on Volaspher A_2 (0.18–0.25 mm, Merck, Darmstadt); carrier gas 35 ml/min N_2, column temperature C = 70°C, retention times t_R [min] = 8.8 (**10**), 9.7 (**1**). – Capillary gas chromatography: Packard model 436 chromatograph, equipped with a Shimadzu Chromatopac C-R6A integrator. A 50 × 0.0001 m fused-silica capillary column having 425500 theoretical plates was employed, which was coated with 0.12 µm silicon oil CP Sil 5CB; 4.0 bar nitrogen pressure, split injection 1:50; C = 80, t_R [min] = 9.65 (**4**), 9.98 (**5**), 19.20 (**1**), 24.53 (**13**). The reported ratios of compounds (Table 1) were calculated from peak areas without corrections by means of specific response factors.

Diethyl ether was distilled under argon (99.998%) from sodium potassium alloy. Sodium amide from Fluka, Buchs, Switzerland, was freed from paraffin oil by washing with petrol ether (30–50°C) and dried under a stream of argon. A sample of 1,1,2,2-tetramethyl-3-methylenecyclopropane (**4**)[37] was obtained from Prof. P. Binger, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr. 3,5-Dihydro-3,3,5,5-tetramethyl-4*H*-pyrazol-4-one (**10**)[8] and methyltriphenylphosphonium bromide[38] were obtained according to known procedures.

Table 2. Chemical shifts (δ values relative to internal tetramethylsilane) and absolute values of coupling constants [Hz] in 400-MHz proton spectra. The signals are singlets unless specified otherwise. Data reported in the literature are given in square brackets

Cpd.	$=CH_2$	CH_3	NH (broad s)			Solvent
1	4.608	1.207				C_6D_6
	4.868	1.316				C_6D_{12}
	[4.91	1.35				CCl_4][17]
	[5.00	1.42				$CDCl_3$][20]
13	4.546	1.023	3.41			C_6D_6
	4.690	1.133	3.37			C_6D_{12}
4	5.288	1.122				C_6D_6
	5.114	1.119				C_6D_{12}
	[5.14	1.12				$CDCl_3$][20]
	[5.39	1.12				C_6H_6][6]
	$>CH_2$ (m)	$>C(CH_3)_2$	$=C(CH_3)_2$	^4J	^5J	
5[a]	0.869	1.172	1.78 - 1.80 (m)		1.7[b]	C_6D_6
	0.779	1.138	1.724 (qt) 1.750 (qt)	0.4 0.4	1.5 1.8	C_6D_{12}
	[0.78	1.14	1.72 , 1.74			$CDCl_3$][20]
	[0.85	1.19	1.61 , 1.81			C_6H_6][6]

[a] The isopropylidene group and the protons attached to the cyclopropane ring constitute an $A_3B_3X_2$ spin system. The X_2 part of the spectrum appears as a pseudo septet. The A_3 part and the B_3 part overlap in the spectra obtained from [D_6]benzene solutions. They form triplets of quartets when [D_{12}]cyclohexane is used as solvent. – [b] $1/2 \mid {}^5J_{AX} + {}^5J_{BX} \mid = 1.7$ Hz.

Table 3. Chemical shifts (δ values relative to internal tetramethylsilane) in 100-MHz carbon-13 spectra. Data reported in the literature are compiled in square brackets

Cpd.	H_2C =	C-4	C-3		$>C(CH_3)_2$	$=C(CH_3)_2$	[a]
1	102.61	158.81	89.45		27.34		B
	102.47	159.99	89.67		27.57		C
	[102.9	159.6	89.8		27.3]		D
13	100.52	168.81	64.88		27.90		B
	100.55	169.83	65.30		28.21		C
	H_2C =	C-1	C-2				
4	98.28	154.00	21.38		20.90		B
	98.13	153.95	21.63		20.96		C
	C =	C-1	C-2	C-3			
5	119.73	[b]	16.60	17.52	24.12	22.11 22.13	B
	119.86	128.57	16.89	17.56	24.23	22.00 22.04	C
	[119.6	128.1	16.4	17.2	24.0	21.9]	T

[a] Solvent B: [D_6]benzene, C: [D_{12}]cyclohexane, D: [D_8]dioxane[20], T: [D]trichloromethane[20]. – [b] The signal is hidden under the solvent signal.

3,5-Dihydro-3,3,5,5-tetramethyl-4-methylene-4H-pyrazole (**1**): A suspension of 4.20 g (108 mmol) of sodium amide and 14.3 g (40 mmol) of methyltriphenylphosphonium bromide in 50 ml of ether was stirred under argon for 2 d. The solid was filtered under argon and washed with ether. To the orange-yellow filtrate was added 1.12 g (8.0 mmol) of **10**. After stirring for 2 d, the mixture was poured into 200 ml of water. The solid was filtered and washed with pentane. The filtrate was washed with a saturated solution of $NaBH_4$ in water which was reextracted with four 50-ml portions of pentane. Drying with sodium sulfate, removal of the solvent by distillation through a 30-cm Vigreux column at ambient pressure and sublimation of the residue at 40°C (bath temperature)/17 Torr onto a finger cooled to –40°C yielded 600 mg (56%) of colourless crystals, m.p. 34–35°C [ref.: 20%, m.p. 34.5–35.5°C[17]; 76%, m.p. 35.0–36.2°C[8]; 33%[18]; 75%[10]; 75%, colourless liquid[39]]. – IR (film): $\tilde{\nu}$ = 3070 cm^{-1} (=C–H), 1670 (C=C), 1548 (N=N). – MS: m/z (%) = 139 (1) [M^+ + 1], 110 (32) [M^+ – N_2], 95 (95) [M^+ – Me – N_2], 67 (100), 55 (45), 41 (73), 39 (41).

2,3,4,5-Tetrahydro-3,3,5,5-tetramethyl-4-methylene-1H-pyrazole (**13**): A mixture of 138 mg (1.0 mmol) of **1**, 380 mg (5.0 mmol) of zinc dust, and 6 ml of 2 M aqueous sodium hydroxide solution was stirred under argon for 12 h at 0°C and 2 h at 20–25°C. The excess zinc was removed by centrifugation. Extraction with three 1-ml portions of pentane, removal of the solvent in vacuo (200 Torr), and drying of the residue at 0.03 Torr afforded 140 mg (quant.) of colourless crystals, m.p. 75–76°C. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1} (=C–H). – MS: m/z (%) = 140 (6) [M^+], 125 (100) [M^+ – Me], 110 (38), 95 (8), 69 (40), 56 (11), 55 (16).

$C_8H_{16}N_2$	Exact mass	Calcd.	140.1313
		Found	140.1317

Photolysis Experiments: The NMR sample tubes containing 0.6–0.7 M solutions of **1** were carefully degassed by several freeze-pump-thaw cycles and sealed under a vacuum of 10^{-5} Torr or flushed with dry nitrogen or oxygen for 10 min. When pentane was used as solvent, 0.1 ml of [D_{12}]cyclohexane was added as an internal lock for recording the NMR spectra. 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 5-mm cut-off filters, type WG 345 or WG 295, from Schott & Gen., Mainz, were used. In experiments at low temperatures, the sample tube was placed in a 1-cm quartz cuvette filled with methanol. The cuvette was held in a copper block which was positioned in a quartz dewar equipped with Suprasil quartz windows and a gas inlet for flushing with dry nitrogen. Cooling of the copper block was provided by a thermostat. The temperature of the cuvette was measured before and after the experiment. The proportions of starting material and products were calculated from integrations of proton signals or peak areas in gas chromatograms.

CAS Registry Numbers

1: 55790-78-8 / **4**: 54376-39-5 / **5**: 1121-36-4 / **10**: 30467-62-0 / **13**: 132540-40-0 / methyltriphenylphosphonium bromide: 1779-49-3

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