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Photochemistry of 3,3-cyclopentyl-3H-pyrazole

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Abstract

Irradiation of 3,3-cyclopentyl-3H-pyrazole yields spiro[2,4]hept-1-ene, vinylidenecyclopentane, and 1-vinylcyclopentene by direct intramolecular rearrangements from the excited diazoalkene (54%) and by competitive formation and subsequent rearrangement of the corresponding vinylcarbene. © 1997 Elsevier Science S.A. All rights reserved.

Keywords: 3,3-cyclopentyl-3H-pyrazole

1. Introduction

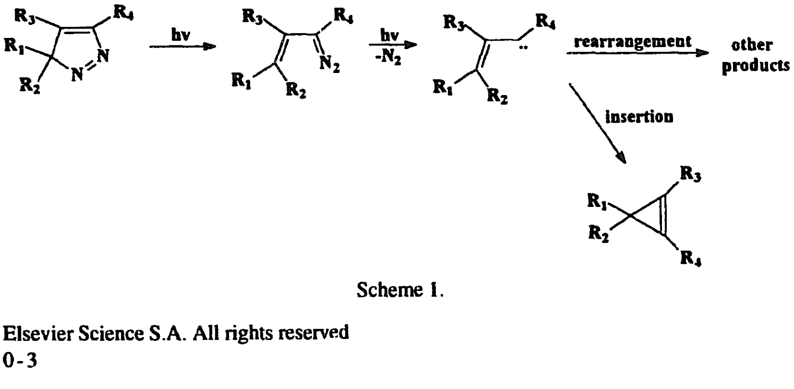
The photochemical reaction of 3H-pyrazoles (pyrazolenines) is an area of continuing interest [1]. Irradiation of the 3H-pyrazoles results in the formation of cyclopropenes and some rearrangement products. A conventional mechanism accounting for all products observed is shown in Scheme 1 [2]. The first step presumably yields the diazoalkenes, and subsequent loss of nitrogen forms the vinylcarbene intermediates. The carbene intermediates can then undergo either insertion or rearrangement to form the final products. In recent years, much information has been obtained on the photolysis of nitrogenous precursors, the diazirine and the diazo compounds [3–5]. Various experimental results suggest that the mechanism of the photolysis of the nitrogenous precursors might be more complicated than a simple carbene route. A literature survey revealed that the spiro-3H-pyrazole has not hitherto been synthesized, nor has its photochemical reaction been investigated. We report herein a convenient procedure for the synthesis of a new spiro-3H-pyrazole, 3,3-cyclopentyl-3H-pyrazole, and the investigation of the photochemistry of this new compound in the presence or absence of some trapping agents.

2. Experimental details

Gas chromatography (GC) analyses were performed on an HP 5890 chromatograph using a 22 ft, 10% sp-2100 and an HP-5 (30 m) capillary column. Mass spectra were recorded using an HP 5890 and 5970 MSD. IR spectra were obtained on a Perkin-Elmer 2000 FT-IR. ^{1}H NMR spectra were determined on a Bruker AC-250 spectrometer in $CDCl_3$ with TMS as an internal standard.

2.1. Materials

$^2\Delta$-Pyrazoline [6] and the authentic photoproducts, spiro[2,4]hept-1-ene [7], 1-vinylcyclopentene [7], vinylidenecyclopentane [7], and the trapping photoproduct, 1-cyclopentylidene-2,2,3,3-tetramethyl-cyclopropane [8],



Scheme 1.

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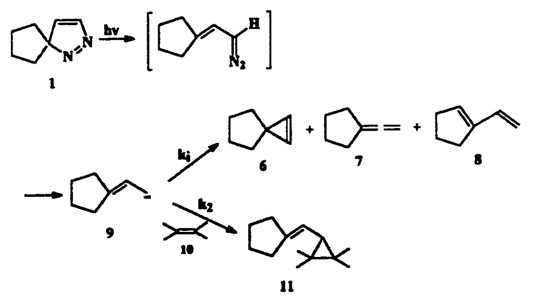


Scheme 2.

were synthesized according to the procedures described in the literature.

2.1.1. *N-Tosyl-²Δ-pyrazoline*

To a stirred and cooled (0 °C) solution of ²Δ-pyrazoline (12.4 g, 0.10 mol) and pyridine (10 ml) in dry THF (30 ml), a solution of *p*-toluenesulfonyl chloride (19.1 g, 0.10 mol) in THF (30 ml), was added. The reaction mixture was then stirred overnight. The mixture was diluted with water and extracted with ether. The ether layer was washed with 5% hydrochloric acid and the organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel with ether/CH_2Cl_2/*n*-hexane = 1:1:3 as the eluent to give the pure product: 22.2 g, 80% yield, m.p. 125–126 °C. The spectral data are as follows. ¹H NMR ($CDCl_3$) δ: 1.46–1.79 (m, 6H), 2.34 (s, 3H), 2.38–2.39 (m, 2H), 2.68 (m, 2H), 6.84 (s, 1H), 7.22 (d, 2H, J = 8.3 Hz), 7.66 (d, 2H, J = 8.3 Hz). IR (neat): 2957, 1596, 1348, 1159, 1109, 964 cm^{-1}. MS *m/z* (%): 278 (M^+, 15), 236 (10), 214 (10), 185 (15), 172 (100), 91 (61). Anal. Calc. for $C_{14}H_{18}N_2O_2S$: C, 60.43; H, 6.48; N, 10.07; S, 11.51. Found: C, 60.31; H, 6.54; N, 10.06; S, 11.59.

2.1.2. *3,3-Cyclopentyl-3H-pyrazole*

To a stirred solution of *N*-tosyl-²Δ-pyrazoline (27.8 g, 0.10 mol) in THF (180 ml) was added potassium *tert*-butoxide (11.8 g, 0.11 mol), and the mixture was heated to reflux for 30 min. The mixture was filtered and the filtrate was evaporated in vacuo to give an oily residue. The residue was purified by column chromatography on silica gel with ether/*n*-hexane = 2/3 as the eluent to give the pure product: 2.92 g, 24% yield. IR (neat): 2962, 2872, 1642, 1424, 1305, 944 cm^{-1}. ¹H NMR ($CDCl_3$) δ: 1.79–2.28 (m, 8H), 6.90 (d, 1H, J = 3.2 Hz), 7.44 (d, 1H, J = 3.2 Hz). MS *m/z* (%): 122 (M^+, 34), 94 (100), 81 (5). Anal. Calc. for $C_7H_{10}N_2$: C, 68.85; H, 8.20; N, 22.95. Found: C, 68.25; H, 8.47; N, 22.23.

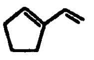
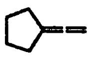
2.1.3. *1-Cyclopentylideneacetalcohol*

To a solution of cyclopentylidene-acetaldehyde (0.44 g, 4.0 mmol) in methanolic cerium(III) chloride (11 ml, 0.4 M, 4.4 mmol) was added sodium borohydride (0.19 g, 5.0 mmol). The reaction mixture was stirred for 10 min. The excess of $NaBH_4$ was destroyed with acetone (5 ml); and the mixture was then diluted with water and extracted with ether. The resulting material was purified by column chromatography on silica gel with *n*-hexane/CH_2Cl_2 = 1/4 as the eluent to give the pure product: 0.41 g, 91% yield. IR (neat): 3323, 2954, 2868, 1432, 1002 cm^{-1}. ¹H NMR ($CDCl_3$) δ: 1.54 (brs, 1H), 1.57–1.73 (m, 4H), 2.23–2.30 (m, 4H), 4.13 (d, 2H, J = 6.6 Hz), 5.51 (m, 1H). MS *m/z* (%): 112 (M^+, 13), 97 (14), 94 (45), 83 (34), 79 (100), 68 (19), 67 (33).

2.1.4. *1-Cyclopentylidene methoxyether*

To a solution of 1-cyclopentylideneacetalcohol (0.5 g, 4.5 mmol) in dimethyl sulfoxide (20 ml) was added powdered potassium hydroxide (0.43 g, 7.6 mmol). After 10 min of stirring, methyl iodide (1.5 g, 10.6 mmol) was added. After an additional 2 h of stirring, distilled water (100 ml) was added, and extracted with methylene chloride. The extract was dried, and evaporated. The residue was purified by column chromatography on silica gel with *n*-hexane/ether = 2/1 as the eluent to give the pure product: 0.11 g, 24% yield. IR (neat): 2955, 1456, 1114 cm^{-1}. ¹H NMR ($CDCl_3$) δ: 1.59–1.74 (m, 4H), 2.22–2.32 (m, 4H), 3.33 (s, 3H), 3.90 (d, 2H, J = 6.9 Hz), 5.44 (m, 1H). MS *m/z*

Table 1
Photolysis of 3,3-cyclopentyl-3H-pyrazole in 2,3-dimethyl-2-butene–CH_2Cl_2

(M)	Adduct (%)	Rearrangement (%)				1/[TME]	[Ad]/[Re]	[Re]/[Ad]
[TME]					Re. total			
0	–	85.1	9.3	5.6	100.0	–	–	–
0.084	2.4	70.9	17.1	9.6	97.6	11.900	0.025	40.667
0.168	4.6	70.3	15.5	9.6	95.4	5.950	0.048	20.739
0.335	8.8	68.2	13.5	9.5	91.2	2.990	0.096	10.364
0.670	15.2	64.7	11.4	8.7	84.8	1.490	0.180	5.579
1.340	19.5	62.4	9.9	8.2	80.5	0.746	0.242	4.128
2.350	25.8	57.7	9.0	7.5	74.2	0.426	0.348	2.876
3.350	29.6	55.6	8.8	6.0	70.4	0.298	0.421	2.378
5.030	34.0	51.2	8.6	6.2	66.0	0.198	0.515	1.941
6.670	39.5	48.3	7.9	4.3	60.5	0.150	0.653	1.532

(%): 126(M^+, 14), 111 (17), 97 (63), 94 (59), 79 (100), 67 (45).

2.1.5. *1-Methoxy-1-vinylcyclopentane*

To a suspension of NaH (0.28 g, 11.2 mmol) in anhydrous THF (10 ml) at 50 °C was added methyl iodide (1.90 g, 13.4 mmol). Then a solution of 1-vinylcyclopentanol (1.0 g, 8.9 mmol) in THF(5 ml) was added dropwise over 30 min. The mixture was heated to reflux for 30 min. The mixture was cooled, treated with water (10 ml), and extracted with ether (3 × 10 ml). The combined organic layers were dried and evaporated. The residue was purified by column chromatography on silica gel with *n*-hexane/ether = 10/1 as the eluent to give the product. IR (neat): 2963, 2360, 1737, 1457, 1069, 917 cm^{-1}. ^1H NMR($CDCl_3$) δ: 0.60–0.82 (m, 8H), 2.09 (s, 3H), 4.11 (m, 2H), 4.82 (m, 1H). MS *m/z* (%): 126 (M^+, 17), 111 (94), 97 (100), 67 (38).

2.2. *General photolysis procedure*

2.2.1. *In CH_2Cl_2*

A mixture of 3,3-cyclopentyl-3H-pyrazole (0.12 g, 1.0 mmol) and decane (0.03 g) as an internal standard in 20 ml of CH_2Cl_2 was stirred and purged with nitrogen for 1 h. The mixture was then irradiated with a Hanovia 450 W medium pressure mercury lamp through a pyrex tube at 0 °C for 45 min. During photolysis, standard aliquots of 0.5 ml were taken at intervals. Each aliquot was subjected to GC and GC–MS analysis.

2.2.2. *In CH_2Cl_2 and TME*

A mixture of 3,3-cyclopentyl-3H-pyrazole (0.12 g, 1.0 mmol), decane (0.05 g), and various amounts of 2,3-dimethyl-2-butene (TME, 0.08–6.67 M) in 20 ml of CH_2Cl_2 were stirred for one hour under N_2. The photoproducts were identified by comparison of their GC retention times and mass spectral data with those of authentic samples.

2.2.3. *In CH_2Cl_2 and MeOH*

A mixture of 3,3-cyclopentyl-3H-pyrazole (0.12 g, 1.0 mmol), decane (0.03 g), and various amounts of CH_3OH (0.25–20.01 M) in 20 ml of CH_2Cl_2 were stirred and purged with nitrogen for 1 h. The mixture was photolyzed and the products were analyzed as previously described.

3. Results and discussion

3,3-Cyclopentyl-3H-pyrazole (1) was synthesized by the sequence of reaction steps indicated in Eq. (1). The cyclopentylidene-acetaldehyde (2) was treated with hydrazine hydrate to yield $^2\Delta$-pyrazoline (3). Since 3 was unstable, conversion of 3 to *N*-tosyl-$^2\Delta$-pyrazoline (4) was necessary. The 3 was effectively converted to 4 by treatment with tosyl chloride and pyridine. Finally, elimination of the tosyl group from 4 by reacting with potassium *tert*-butoxide yielded 1

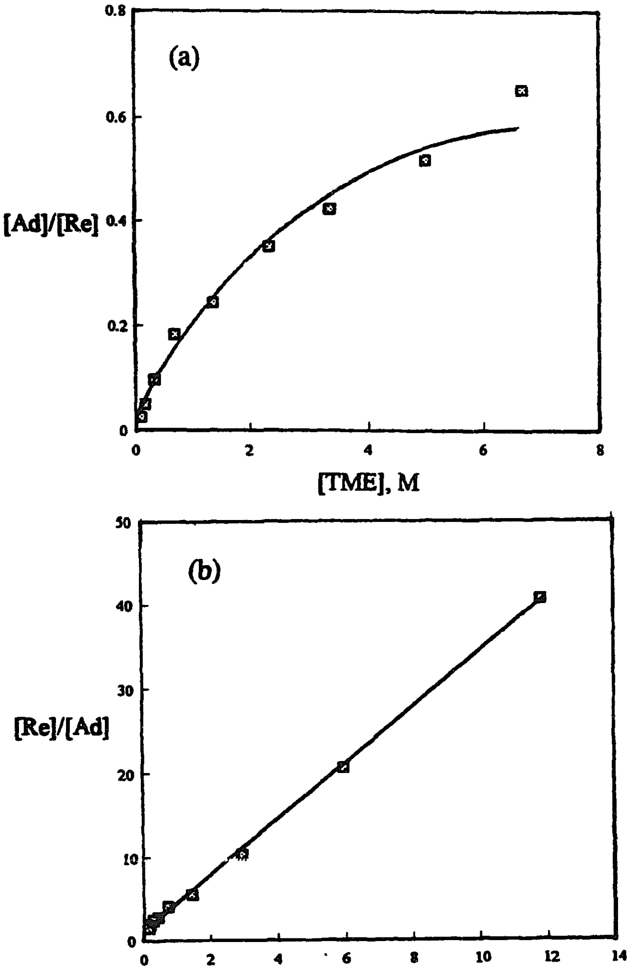
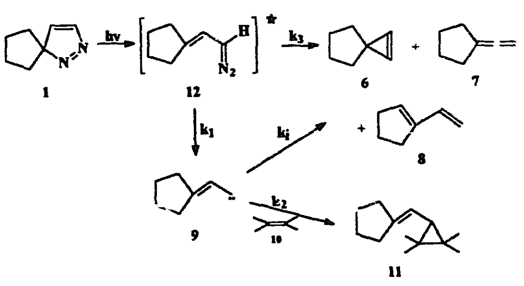
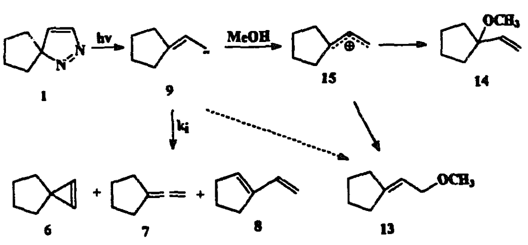


Fig. 1. (A) Addition-to-rearrangement product ratio [11]/([6] + [7] + [8]) vs. [TME] for the photolysis of 1 in 2,3-dimethyl-2-butene (TME). (B) Rearrangement-to-addition product ratio ([6] + [7] + [8])/[11] vs. 1/[TME] for the photolysis of 1 in 2,3-dimethyl-2-butene(TME).

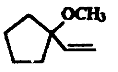
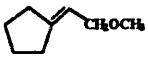
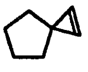
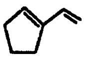
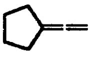


Scheme 3.

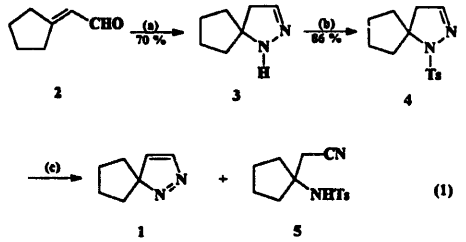


Scheme 4.

Table 2
Photolysis of 3,3-cyclopentyl-3H-pyrazole in methanol–CH_2Cl_2

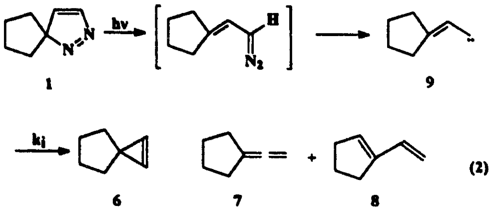
(M)	Adduct (%)		Rearrangement (%)				1/[MeOH]	[Ad]/[Re]	[Re]/[Ad]
[MeOH]						Re. total			
0	-	-	82.7	10.7	6.6	100.0	-	--	-
0.252	4.0	7.2	61.7	16.5	10.6	88.8	3.968	0.127	7.900
0.504	4.4	12.4	58.6	15.8	8.8	83.2	1.984	0.202	4.952
1.005	5.9	17.4	56.3	14.0	6.4	76.7	0.995	0.304	3.292
2.010	11.0	20.8	50.6	13.1	4.5	68.2	0.498	0.366	2.145
7.500	13.6	23.3	47.0	12.1	4.0	63.1	0.133	0.585	1.710
15.090	14.8	23.9	46.3	11.1	3.9	61.3	0.066	0.629	1.591
20.010	16.2	24.5	45.4	10.0	3.9	59.3	0.050	0.686	1.457

and 5 in yields of 24% and 76% respectively ((a) $NH_2NH_2 \cdot H_2O$; (b) TsCl/pyridine; (c) *t*-BuOK).



(1)

Irradiation of 3,3-cyclopentyl-3H-pyrazole in CH_2Cl_2 at 0 °C led to the formation of the diazo compound, which was indicated by the solution turning red and an IR spectrum ($\bar{\nu}=2056$ cm^{-1}). Further irradiation of the diazo compound at 0 °C yielded spiro[2,4]hept-1-ene (6, 35%), vinylidenecyclopentane (7, 2%), and 1-vinylcyclopentene (8, 4%) (Eq. (2)).



(2)

The photoproducts spirocyclopropene 6, allene 7, and diene 8 apparently arise from the cyclization, 1,2-H shift, and 1,4-H shift respectively in the photolytically generated vinycarbene 9. When the irradiation of 1 was carried out in the presence of excess tetramethyl ethylene (TME) (10), the cyclization and H shift were suppressed concomitantly with the formation of the additional product 1-cyclo-pentylidene-2,2,3,3-tetramethylcyclopropane (11) (Scheme 2).

In this system, the ratio of the product yield of the intermolecular addition (Ad) to the product yields of the intramolecular rearrangement (Re), i.e. [11]/([6]+[7]+[8]), increases with increasing alkene trap (Table 1). However, the correlation is strongly curved (Fig. 1(A)). This behavior is inconsistent with a simple competitive mechanism, e.g., the vinyl carbene 9 partitions between intermolecular addition to the alkene and intramolecular rearrangement. Such a mechanism would exhibit a linear dependence of [Ad]/[Re] on [alkene].

By contrast, the inverse correlation of [Re]/[Ad] product ratio vs. 1/[alkene] was found to be linear (Fig. 1(B)). To account for the observed results, a mechanism similar to Moss and Ho's diazirine case [9] is proposed (Scheme 3).

A second product-forming intermediate, the excited diazoalkene 12, is introduced. The excited diazoalkene 12 not only gives the vinylcarbene (K_1) but also directly yields the intramolecular rearrangement products 6–8 (K_3). The vinylcarbene 9 either rearranges to the intramolecular products 6–8 (K_i) or adds to the alkene (K_2). The analytical expression corresponding to the mechanism of Scheme 3 is

$$\frac{[\mathrm{Re}]}{[\mathrm{Ad}]}=\frac{k_3}{k_1}+\frac{k_i(k_1+k_3)}{k_1k_2[\mathrm{alkene}]} \tag{3}$$

According to Eq. (3), the *Y*-intercept of the correlation in Fig. 1(B) represents the ratio of rate constant (K_3/K_1) for the direct intramolecular rearrangement (with no nitrogen loss) of 12 to products 6–8 relative to the simple nitrogen loss conversion of 12 into the vinylcarbene 9, from which the intramolecular rearrangement products also arise.

The observed *Y*-intercept is calculated to be 1.17 ± 0.41 ($r=0.999$). The experimental (K_3/K_1) ratio translates into 54% excited diazoalkene incursion and 46% vinylcarbene parentage for photoproducts 6–8.

Photolysis of 3,3-cyclopentyl-3H-pyrazole in methanol at 0 °C yielded not only the intramolecular rearrangement photoproducts 6–8 but also the carbenic O–H insertion products cyclopentylidene-methoxyether (13) and 1-methoxy-1-vinylcyclopentane (14). The product distribution ratio between 13 and 14 was found to be 2:1. Probably, 13 and 14 would be formed via a delocalized cationic intermediate 15 which was generated by the reaction of carbene 9 with methanol (Scheme 4) [10]. It is not clear whether the uneven distribution of product observed with 13 is due to ion pairing or to competing reactions of the carbene 9.

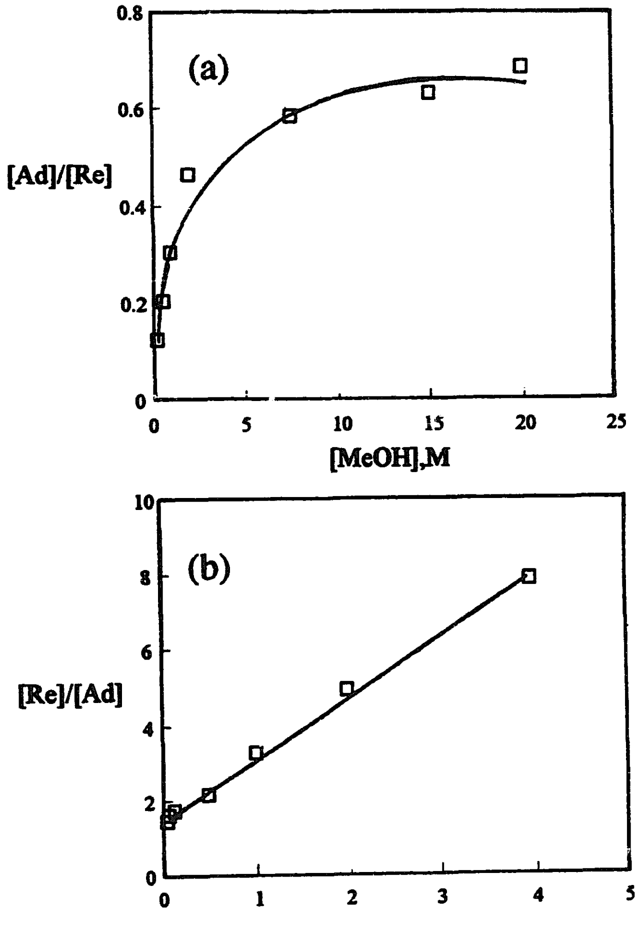
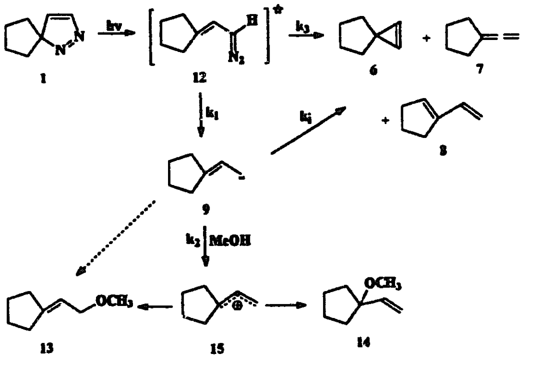


Fig. 2. (A) Addition-to-rearrangement product ratio ([13]+[14])/([6]+[7]+[8]) vs. [MeOH] for the photolysis of 1 in methanol. (B) Rearrangement-to-addition product ratio ([6]+[7]+[8])/([13]]+[14]) vs. 1/[MeOH] for the photolysis of 1 in methanol.



Scheme 5.

When the irradiation of 1 was carried out in CH_2Cl_2 with the added trapping agent CH_3OH, the intramolecular rearrangement products were suppressed concomitantly with the formation of the additional products 13 and 14 (Table 2). Analysis of the ratio of the insertion products to the rearrangement products as a function of [CH_3OH] also indicates two pathways for 6–8 production (Fig. 2(A) and (B)). A second product-forming intermediate, the excited diazoalkene 12, is also proposed (Scheme 5). The excited diazoalkene 12 not only gives the vinylcarbene (K_1) but also directly yields the intramolecular rearrangement products 6–8 (K_3). The vinylcarbene 9 either rearranges to the intramolecular products 6–8 (K_i) or adds to methanol (K_2). The analytical expression corresponding to the mechanism of Scheme 5 is

$$\frac{[\mathrm{Re}]}{[\mathrm{Ad}]}=\frac{k_3}{k_1}+\frac{k_i(k_1+k_3)}{k_1k_2[\mathrm{MeOH}]} \tag{4}$$

According to Eq. (4), the Y-intercept of the correlation in Fig. 2(B) represents the ratio of rate constant (K_3/K_1) for the direct intramolecular rearrangement (with no nitrogen loss) of 12 to products 6–8 relative to the simple nitrogen loss conversion of 12 into the vinylcarbene 9, from which the intramolecular rearrangement products also arise.

The observed Y-intercept is calculated to be 1.48 ± 0.15 ($r = 0.998$). The experimental (K_3/K_1) ratio translates into 60% excited diazoalkene incursion and 40% vinylcarbene parentage for photoproducts 6–8.

Acknowledgements

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