

Base-induced photochemical reaction of cyclopentylideneacetaldehyde tosylhydrazone

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Abstract

Irradiation of base-induced cyclopentylideneacetaldehyde tosylhydrazone affords spiro[2.4]hept-1-ene, vinylidenecyclopentane and 1-vinylcyclopentene by direct intramolecular rearrangements from the excited diazoalkene state (64%) and by competitive formation and subsequent rearrangement of the corresponding vinylcarbene.

Keywords: Photochemical reaction; Cyclopentylideneacetaldehyde; Tosylhydrazone

1. Introduction

The photolysis of nitrogenous precursors such as diazo and diazine compounds is quite general for generating carbene intermediates [1]. The carbene can follow several reaction pathways: rearrangement, addition to an alkene or trapping with a solvent. Various experimental results suggest that the mechanism of the photolysis of nitrogenous precursors might be more complicated than a simple loss of nitrogen to generate a ground state carbene. For example, considerably different product distributions are formed on pyrolysis and photolysis [2,3] and different *E/Z* ratios are observed upon photolysis of nitrogenous precursors in the presence of alkene traps [4].

Carbene chemists have recognized [3,5,6] that these experimental results require a more complex mechanism for the photolysis of nitrogenous precursors, a mechanism that should have at least two pathways by which rearrangement products are formed (a carbene and a non-carbene route).

In this paper we describe our work on the photolysis of the potassium salt of cyclopentylideneacetaldehyde tosylhydrazone in the presence or absence of a trapping alkene and propose a possible mechanism for the formation of the rearrangement photoproducts.

2. Experimental details

Gas chromatography (GC) analyses were performed on a China 8900 chromatograph using a 22 ft 10% SP-2100. Mass spectra were recorded using an HP 5890 and an HP 5970 BMSD. IR spectra were obtained on a Perkin-Elmer 2000 FT-IR. ¹H NMR spectra were determined on a Bruker AC-250 spectrophotometer in CDCl₃ with TMS as an internal standard.

2.1. Materials

Cyclopentylideneacetaldehyde [7] and the authentic photoproducts spiro[2.4]hept-1-ene [8], vinylidenecyclopentane [8] and 1-vinylcyclopentene [8] were synthesized according to the literature procedures. Ethynylcyclopentane was purchased from MTM Research Chemicals Ltd.

Cyclopentylideneacetaldehyde tosylhydrazone. A solution of toluenesulphonylhydrazide (7.8 g, 42 mmol) in 100 ml of hot ethanol was added to a mixture of cyclopentylideneacetaldehyde (5.4 g, 49 mmol) in 500 ml of ethanol. The reaction mixture was stirred for 10 min and stored in a freezer overnight. A yellow precipitate was recrystallized from CH₂Cl₂: 5.38 g, 46% yield, m.p. 121–122 °C. The spectral data were as follows. ¹H NMR (*d*₆-acetone) δ: 1.63–1.95 (m, 4H), 2.35–2.70 (m, 7H), 5.75 (d, 1H, *J* = 10 Hz), 7.23 (d, 2H, *J* = 8 Hz), 7.61 (dd, 3H, *J* = 8, 10 Hz), 9.62 (s, 1H). IR (neat): 3222, 2959, 1647, 1328, 1163 cm⁻¹. MS *m/z* (%): 278 (M⁺, 4), 123 (91), 94 (60), 91 (100), 79 (78), 65 (88).

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Anal. calc. for $C_{14}H_{18}N_{14}SO_2$: C, 60.40; H, 6.47; N, 10.07. Found: C, 60.11; H, 6.50; N, 10.06.

1-Cyclopentylidene-2,2,3,3-tetramethylcyclopropane. To cyclopentyltriphenylphosphonium bromide (2.3 g, 5.54 mmol) in 44 ml of dry ether was added 2.5 ml of *n*-BuLi (6.25 mmol, 2.5 M) in *n*-hexane at 0 °C under N_2 . After stirring for 0.5 h, 2,2,3,3-tetramethylcyclopropanecarboxaldehyde [9] (0.43 g, 3.41 mmol) in 51 ml of dry ether was added. The mixture was stirred for 1 h at 0 °C, then poured into water and extracted with *n*-hexane. The organic layer was dried and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel with *n*-hexane as the eluant to give the pure product: 0.54 g, 89% yield. IR (neat): 2930, 1458, 1378, 1133 cm^{-1} . 1H NMR ($CDCl_3$) δ : 1.05 (s, 6H), 1.17 (s, 6H), 0.83–1.50 (m, 5H), 1.53–1.73 (m, 2H), 2.19–2.29 (m, 2H), 5.09 (d, 1H, $J=9.6$ Hz). MS m/z (%): 178 (M^+ , 68), 163 (100), 135 (27), 121 (53), 107 (93), 93 (72). Anal. calc. for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.30; H, 12.58. HRMS calc. for $C_{13}H_{22}$: 178.1738. Found: 178.1728.

2.2. General photolysis procedure

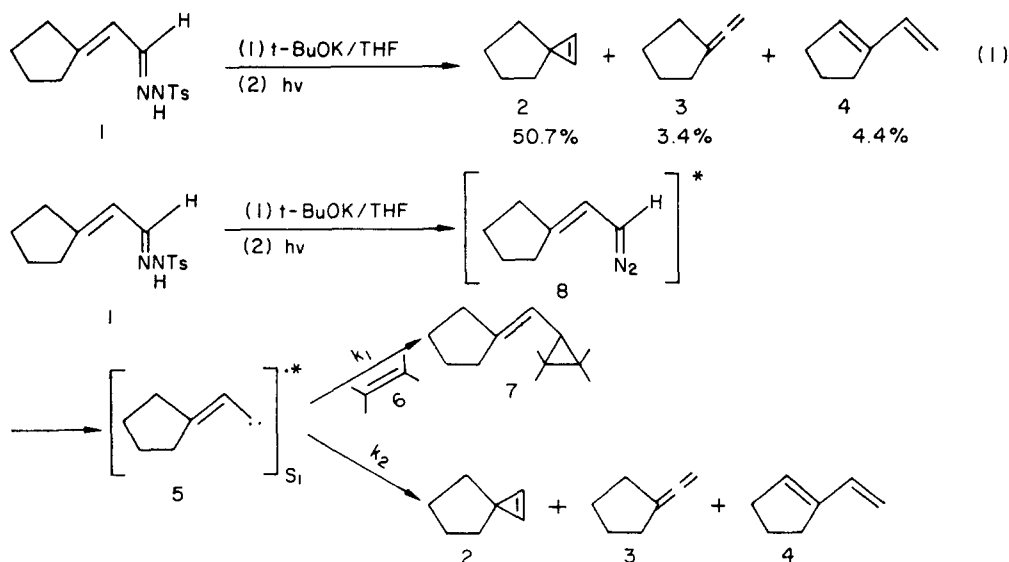
With 'BuOK in THF. A mixture of 0.50 g (1.8 mmol) of cyclopentylideneacetaldehyde tosylhydrazone, 0.3 g (2.7 mmol) of potassium *tert*-butoxide and 0.36 g of decane as an internal standard in 350 ml of dry THF was stirred for 24 h under nitrogen. The reaction mixture gradually turned red and was then irradiated with a Hanovia 450 W medium pressure mercury lamp through a Pyrex immersion vessel at 0 °C for 45 min. During the photolysis, standard aliquots of 0.50 ml were taken at intervals. Each aliquot was washed with 1 ml of water and extracted with 0.50 ml of ether. The ether solutions were subjected to GC and GC–MS analysis.

With 'BuOK in THF and TME. A mixture of cyclopentylideneacetaldehyde tosylhydrazone (0.30 g, 1.1 mmol), potassium *tert*-butoxide (0.18 g, 1.6 mmol), decane (0.10 mmol) and various amounts of 2,3-dimethyl-2-butene (TME, 0.08–6.67 M) in 20 ml of THF were stirred for 24 h under N_2 . The mixture was photolysed in the same way as above. The photoproducts were identified by comparison of their GC retention times and mass spectral data with those of authentic samples.

3. Results and discussion

Irradiation of the potassium salt of tosylhydrazone (1) in THF at 0 °C led to formation of the vinyl diazo compound, which was indicated by the reaction solution turning red [10]. Further irradiation of the vinyl diazo compound at 0 °C yielded spiro[2.4]hept-1-ene (2, 50.7%) as the major product, along with small amounts of vinylidenecyclopentane (3, 3.4%) and 1-vinylcyclopentene (4, 4.4%) (Eq. (1)).

Each product was analysed and identified via GC and GC–MS by comparison of its GC retention time and mass spectral data with those of authentic samples. The photoproducts spirocyclopropene 2, allene 3 and diene 4 apparently arise from the cyclization, 1,2-H shift and 1,4-H shift respectively of the photolytically generated vinyl carbene 5. When the irradiation of 1 was carried out in the presence of excess 2,3-dimethyl-2-butene (6), the cyclization and H shift were suppressed concomitantly with the formation of the addition product 1-cyclopentylidene-2,2,3,3-tetramethylcyclopropane (7) (Scheme 1). The addition product was analysed and identified via GC and GC–MS by comparison of its retention time and mass spectral data with those of an authentic sample.



Scheme 1.

Table 1
Photolysis of cyclopentylideneacetaldehyde tosylhydrazone in 2,3-dimethyl-2-butene-THF

(M) [alkene]	Adduct (%)	Rearrangement (%)				1/[alkene]	[Ad]/[Re]	[Re]/[Ad]
		2	3	4	Re total			
0	–	91.93	5.71	2.36	100	–	–	–
0.084	6.05	72.85	17.58	3.52	93.95	11.900	0.064	15.529
0.168	9.53	80.47	6.05	3.95	90.47	5.950	0.105	9.493
0.335	15.93	66.67	12.87	4.62	84.07	2.990	0.190	5.278
0.670	24.45	62.13	7.41	6.01	75.55	1.490	0.324	3.090
1.340	24.92	59.55	11.40	4.13	75.08	0.746	0.332	3.013
2.350	29.32	60.57	7.25	2.86	70.68	0.426	0.415	2.411
3.350	30.73	58.93	6.13	4.21	69.27	0.298	0.444	2.254
5.030	36.67	55.85	5.04	2.44	63.33	0.198	0.579	1.727
6.670	38.52	54.26	4.46	2.76	61.48	0.150	0.627	1.596

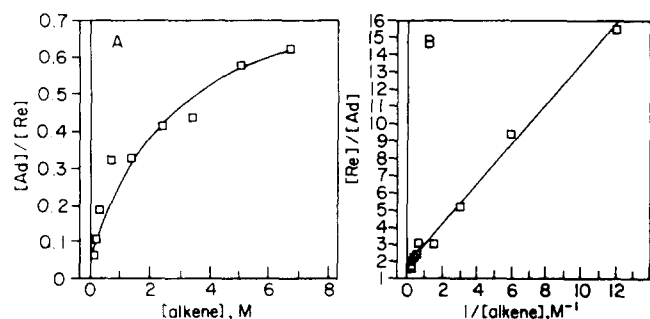


Fig. 1. (A) Addition-to-rearrangement product ratio $[7]/([2]+[3]+[4])$ vs. [alkene] for the photolysis of **1** in tetramethylethylene. (B) Rearrangement-to-addition product ratio $([2]+[3]+[4])/[7]$ vs. $1/[\text{alkene}]$ for the photolysis of **1** in tetramethylethylene (see Table 1).

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. $[7]/([2]+[3]+[4])$, increases with increasing alkene trap, 2,3-dimethyl-2-butene (Table 1). However, the correlation is strongly curved (Fig. 1A). This behaviour is inconsistent with a simple competitive mechanism, e.g. the vinyl carbene **5** partitions between intermolecular addition to the alkene and intramolecular rearrange-

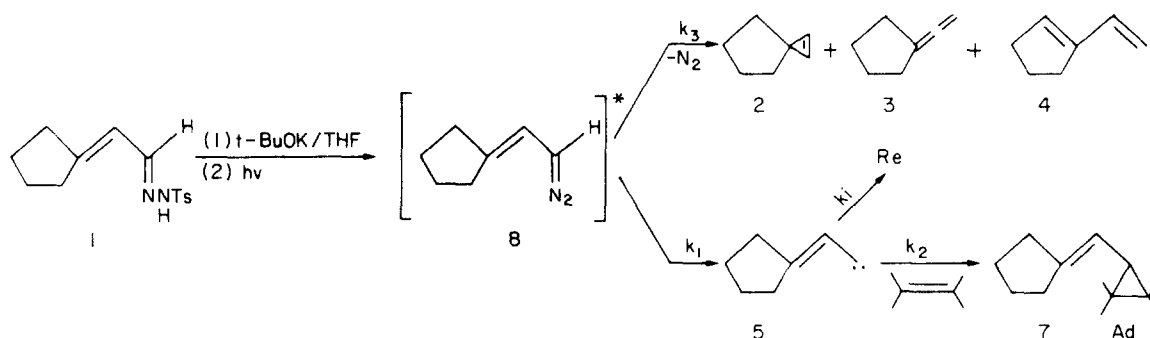
ment. Such a mechanism would exhibit a linear dependence of $[Ad]/[Re]$ on [alkene].

In contrast, the inverse correlation of $[Re]/[Ad]$ product ratio vs. $1/[\text{alkene}]$ was found to be linear (Fig. 1B). To account for the observed results, a mechanism similar to Moss and Ho's diazine case [11] is proposed (Scheme 2). A second product-forming intermediate, the excited diazoalkene **8**, is introduced. The excited diazoalkene **8** not only gives the vinyl carbene (K_1) but also directly affords the intramolecular rearrangement products spirocyclopropane **2**, allene **3** and diene **4** (K_3). The vinyl carbene **5** either undergoes the same intramolecular rearrangement to form the spirocyclopropane **2**, allene **3** and diene **4** (K_i) or adds to the alkene to form the cyclopropane **7** (K_2).

The analytical expression corresponding to the mechanism of Scheme 2 is

$$\frac{[Re]}{[Ad]} = \frac{K_3}{K_1} + \frac{K_i(K_1 + K_3)}{K_1 K_2 [\text{alkene}]} \quad (2)$$

According to Eq. (2), the Y intercept of the correlation in Fig. 1 represents the ratio of rate constants (K_3/K_1) for the direct intramolecular rearrangement (with no nitrogen loss) of **8** to products **2**, **3** and **4** relative to the simple nitrogen loss conversion of **8** into the vinyl



Scheme 2.

carbene 5, from which the intramolecular rearrangement products also arise.

The observed Y intercept is calculated to be 1.76 ± 0.40 ($r=0.994$). The experimental K_3/K_1 ratio translates into 64% excited diazoalkene incursion and 36% vinyl carbene parentage for photoproducts 2, 3 and 4.

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