

A Novel Photofragmentation of 1-Diphenylmethyl-3,3-diphenyl-4-aryl/(2-thienyl)-2-azetidinones

G.S SINGH

*Department of Pharmaceutics, Institute of Technology
Banaras Hindu University
Varanasi-221 005, India*

Photolysis of titled compounds 1-diphenylmethyl-3, 3-diphenyl-4-aryl/(2-thienyl)-2-azetidinones, (I) in dry benzene gave 1,4,4-triphenyl-5-aryl/(2-thienyl)-3-oxo-1,2,4,5-tetrahydrobenzazepins (II), 1,1,2,2-tetraphenylethane (III), diphenylmethane (IV) and aryl nitriles (V). The products have been characterised on the basis of analytical and spectral (UV, IR, PMR and MS) data and the mechanistic route of their formation is suggested.

INTRODUCTION

Although azetidinone is a biologically important heterocycle, a little attention has been paid to its photochemistry. A few examples available in literature report N-C transacylation, e.g., photolysis of 1-phenyl substituted 2-azetidinones lead benzacridone and benzacycloalkenones^{1,2}. The photofragmentation of N-benzhydryl substituted azetidinones leading to diphenylmethane, 1,1,2,2-tetraphenylethane, aryl nitriles and N-benzhydryldiphenylacetamide has been reported³. The present study reveals the effect of UV light (obtained from 200-W Honovia lamp) on 1-diphenylmethyl-3,3,4-triphenyl-, 1-diphenylmethyl-3,3-diphenyl-4-(4-dimethylaminophenyl)-, 1-diphenylmethyl-3, 3-diphenyl-4-(4-methoxyphenyl)- and 1-diphenylmethyl-3, 3-diphenyl-4-(2-thienyl) -2-azetidinones (Ia-d) in dry benzene. The azetidinone ring undergoes novel ring opening and fragmentation leading to 1,4,4-triphenyl-5-aryl/(2-thienyl)-3-oxo-1,2,4,5-tetrahydrobenzazepins (IIa-d), as a major product of this reaction not reported earlier together with starting azetidinones (Ia-d, yield 40-45%), 1,1,2,2-tetraphenylethane (III), diphenylmethane (IV) and corresponding nitriles (Va-d). The paper also describes the plausible mechanism in detail.

RESULTS AND DISCUSSION

The product mixture, obtained from irradiation of dilute solutions of azetidinones Ia-d in dry benzene in nitrogen atmosphere with UV light from 200 W Hanovia lamp, on fractional crystallisation from *n*-hexane-ethanol (1:1) and column chromatography afforded 1,4,4-triphenyl-5-aryl-3-oxo-1, 2,4,5-

tetrahydrobenzazepins (IIa-d, yield 15-25%), 1,1,2,2-tetraphenylethane (III, yield 5-8%, m. pt. and mix. m. pt. 206°C), diphenylmethane (IV, yield 10-15%) and the starting azetidines Ia-d in 45-50% yields. The IR spectra of the crude product mixtures exhibited a strong absorption band at $2265 \pm 5 \text{ cm}^{-1}$ indicating the presence of nitrile group. The presence of corresponding aryl nitriles (Va-c) was supported by comparison of their R_f values with that of authentic samples. The products III, IV and starting azetidines Ia-d were identified on the basis of comparison (underpressed mix m. pt and/or Co-IR) with authentic samples prepared according to reported methods⁴⁻⁸. Tetrahydrobenzazepins IVa-d were characterised on the basis of analytical (Table 1) and spectral (UV, IR, PMR and MS) data (Table 2). The IR spectra of IIa-d in nujol were characterised by two medium and strong absorption bands respectively at 3280 ± 20 (N-H) and $1640 \pm 5 \text{ cm}^{-1}$ (seven membered heterocyclic amide carbonyl).

TABLE 1
PHYSICAL DATA OF BENZAZEPINS (IIa-d)

Compd.	Ar	Yield (%)	m. pt. (°C)	Mol. formula	Found % (Calcd)		
					C	H	N
IIa	C ₆ H ₅	15	271	C ₃₄ H ₂₇ NO	87.40 (87.74)	5.84 (5.80)	3.25 (3.01)
IIb	C ₆ H ₄ N(CH ₃) ₂ - <i>p</i>	25	200	C ₃₆ H ₃₂ N ₂ O	85.09 (85.04)	6.52 (6.29)	5.76 (5.51)
IIc	C ₆ H ₄ OCH ₃ - <i>p</i>	18	196	C ₃₅ H ₂₉ NO ₂	84.53 (84.85)	5.55 (5.86)	2.83 (2.83)
II d	2-Thienyl	18	165	C ₃₂ H ₂₅ NOS	81.93 (81.52)	5.67 (5.30)	3.17 (2.95)

In the PMR spectra C₁ proton appears as doublet at δ 5.9 ppm which becomes singlet after D₂O shake. The appearance of N-H proton as a doublet and conversion of C₁ proton from doublet to singlet after D₂O shake clearly indicates that they are in vicinity.

The most plausible route for the formation of products is depicted in Scheme I. Photofragmentation of the N-C bond (1,4) of azetidines Ia-d may give rise to biradical *a*. The intramolecular hydrogen transfer in *a* may lead to another biradical *b* (more stable than *a* due to conjugation with two phenyl rings) which may recombine to give tetrahydrobenzazepins IIa-d. Similar biradicals have been proposed earlier in the photolysis of 1-phenyl substituted azetidines leading to benzacycloalkenones¹. The cleavage of N-diphenylmethyl bond of Ia-d may give rise to diphenylmethyl radical *c* and an amido radical *d*. Dimerisation of radical *c* would lead to 1,1,2,2-tetraphenylethane (III). Alternatively radical *c* may abstract a hydrogen atom from the amido radical *d* to form diphenylmethane (IV) and 3,3-diphenyl-4-aryl-1, 4-azetin-2-one. The cleavage of C-C and C-N bonds in latter

may yield aryl nitriles (Va-d) and diphenylketene which, however, could not be isolated or trapped even by addition of ethanol and aniline as it is known to be quite reactive and may undergo either photodecomposition or photopolymerisation⁷.

TABLE 2
SPECTRAL DATA OF BENZAZEPINS (IIa-d)

Compd. No.	IR (Nujol, cm^{-1})		UV (EtOH, nm)	(PMR DMSO- d_6)	Mass $m/z(\text{M}^+)$
	$\nu(\text{N-H})$	$\nu(\text{C-O})$			
IIa	3325	1630	243,248,254, 259,262,265, 268.	7.29 (<i>m</i> , 24H, aromatic), 6.91 (<i>d</i> ,1H, NH, D_2O exch.), 6.50 (<i>s</i> , 1H, CH), 5.90 (<i>d</i> , 1H, CH, singlet after D_2O shake)	461
IIb	3250	1640	240,250,256, 260,266,270	7.10 (<i>m</i> , 23 H, aromatic), 8.10 (<i>d</i> , 1H, NH, D_2O exch.), 5.90 (<i>d</i> , 1H, CH, singlet after D_2O shake), 5.30 (<i>s</i> , 1H,CH), 2.23 (<i>s</i> ,6H, two N- CH_3)	508
IIc	3250	1640	248,253,260, 266,269	6.95 (<i>m</i> , 23H, aromatic), 8.0 (<i>d</i> ,1H,NH, D_2O exch.), 5.84 (<i>d</i> ,1H,CH, singlet after D_2O shake), 5.24 (<i>s</i> , 1H,CH), 4.03 (<i>s</i> , 3H, OCH_3)	495
IIId	3325	1630	250,253,255, 260,266,269	7.13 (<i>m</i> ,23H,aromatic), 6.90 (<i>d</i> ,1H,NH, D_2O exch.), 6.40 (<i>s</i> ,1H,CH), 5.84 (<i>d</i> ,1H,CH, singlet after D_2O shake)	471

EXPERIMENTAL

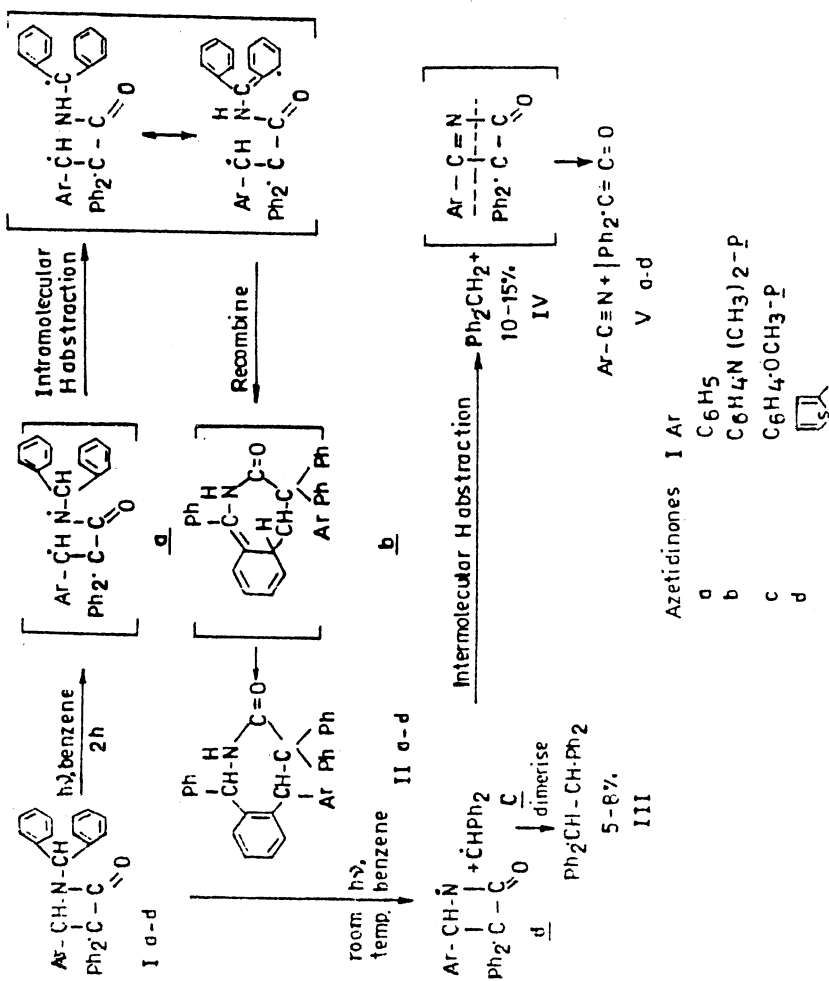
Melting points were determined on a Büchi apparatus and are uncorrected. UV spectra were recorded on a Cary-14 spectrophotometer, IR spectra on a Perkin-Elmer 621 spectrophotometer and PMR spectra on a Jeol FX 90 Q spectrometer using TMS as an internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer model RMU-6E spectrometer.

Azetidinones Ia-d were prepared by the reaction of azibenzil with respective imines by reported methods⁶⁻⁸

General Procedure

A dilute solution of azetidinones Ia-d (1 m mole) in dry benzene (320 ml, thiophene free) was irradiated with UV light from a 200-W medium pressure Hanovia lamp for 2 hrs in a stream of nitrogen. Three such runs were combined and solvent removed under reduced pressure. The IR spectrum of the residual

SCHEME - 1



matter exhibited a band at 2265 cm^{-1} (C-N) and the TLC analysis (comparison of R_f value with authentic samples) indicated the presence of aryl nitriles (Va-c). The residual matter was triturated with *n*-hexane-ethanol (1:1) mixture (10 ml). The solid obtained was crystallised from ethanol to give azetidinones (Ia-d) and tetrahydrobenzazepins (IIa-d). The mother liquor was chromatographed on a neutral alumina column (40 gm, $1.5 \times 20\text{ cm}^2$) using *n*-hexane as eluant. Evaporation of solvent under reduced pressure and crystallisation of residue with *n*-hexane gave 1,1,2,2-tetraphenylethane (III). The liquid product obtained after concentration of the filtrate was identified as diphenylmethane (IV).

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REFERENCES

1. G. Ege and E. Beisiegel, *Angew. Chem.*, **80**, 316 (1968).
2. M. Fieser and A. Mathens, *Chem. Ber.*, **102**, 316 (1968).
3. A.K. Upadhyay and K.N. Mehrotra, *Indian J. Chem.*, **27B**, 944 (1989).
4. J.F. Norris, R. Thomas and B.M. Brown, *Chem. Ber.*, **43**, 2959 (1910).
5. W.W. Hartman and R. Phillips, *Organic Synthesis*, Coll. Vol. II, p. 232 (1950).
6. K.N. Mehrotra and S.B. Singh, *Indian J. Chem.*, **19B**, 702 (1980).
7. _____, *Bull. Chem. Soc. (Japan)*, **54** 1838 (1981).
8. G.S. Singh and S.N. Pandeya, *J. Chem. Engg. Data*, **32**, 278 (1987).
9. H. Nozaki, M. Nakano and K. Kondo, *Tetrahedron*, **22**, 477 (1966).

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