Microwave Specific Wolff Rearrangement of α-Diazoketones and Its Relevance to the Nonthermal and Thermal Effect[†]

Surendra G. Sudrik,*[,‡] Sambhaji P. Chavan,[‡] K. R. S. Chandrakumar,[§] Sourav Pal,[§]
Sadgopal K. Date,[§] Subhash P. Chavan,[‡] and Harikisan R. Sonawane*[,‡,||]

Division of Organic Chemistry: Technology, and Physical Chemistry Division,
National Chemical Laboratory, Pune-411 008, India

spchavan@dalton.ncl.res.in

Received September 25, 2001

α-Diazoketones possess high electric dipole moments, as a consequence of the dipolar nature of the diazocarbonyl functional group. The vectorial analysis, theoretical calculations (PM3 and ab initio), and literature reports based on experimental and theoretical calculations reveal a higher dipole moment for the *Z*-configuration of the diazo functional group. Microwave irradiation of α-diazoketone (**1a**−**m**) (Figure 1) promotes Wolff rearrangement specifically via the *Z*-configuration in excellent yields. The dielectric properties of the solvent govern the course of the microwave rearrangement. 3-Diazocamphor (**1m**) on microwave irradiation in benzylamine exhibits nonthermal effects to furnish exclusively the Wolff rearrangement product (**4m**), equivalent to its photochemical behavior. In the presence of an aqueous medium, through solvent heating predominates, leading to the formation of a tricyclic ketone (**5**) as the principal product, arising from an intramolecular C−H insertion. This behavior is similar to its known thermal and transition metal catalyzed reactivity pattern.

Wolff rearrangement[1] of α-diazoketones is an integral part of the well-known Arndt−Eistert one-carbon homologation of carboxylic acids as well as providing an efficient route to the ring-contracted compounds from cyclic α-diazo carbonyl compounds. Literature is replete with its application in organic synthesis.[1,2] The rearrangement involves specific 1,2-shift, accompanying or following loss of dinitrogen, to ketene via a transient free keto-carbene intermediate. The reaction can be initiated thermally,[3] photochemically,[4] by transition metal catalysis,[5,6] or by ultrasound in the presence of silver ions.[7] Among these, thermolysis is used less frequently than the other techniques despite simplicity in operational conditions due to the several disadvantages associated with conducting the reaction at higher temperature (in the vicinity of 180 °C) such as thermal instability of the ring-contracted products or ketene intermediates and other competing side reactions of carbene occurring at lower temperatures, resulting in the overall poor yield of the rearranged products. These disadvantages were largely overcome by photolysis of the diazocarbonyl functional group in the ultraviolet region ($\lambda \sim 300$ nm); however, a limit is reached when either the product or diazocarbonyl substrates contain other photolabile groups. Among transition metal catalysis, an efficient procedure developed by Newman et al.[5] comprising silver ion catalysis in the presence of triethylamine under homogeneous conditions is generally preferred.

Recent years have witnessed the advent of microwave dielectric heating as the superior technique over the conventional conduction, convection, and radiation modes of heating. Several organic reactions[8] were performed in the presence of microwave absorptive solvents or in the presence of additives such as transition metal salts and completed in minutes with good yields due to the tremendous acceleration in the rate of reaction. Furthermore, with few exceptions[9] the product selectivity obtained in the conventional thermal mode of the reaction remain unchanged. Recent review articles[10] give an

---

[†] Dedicated to Prof. G. S. Sudrik, VJTI, Mumbai, India.

[‡] Division of Organic Chemistry: Technology.

[§] Physical Chemistry Division.

[||] Fax: 91-20-5893614.

(1) For reviews, see: (a) Ye, T.; Mckervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. (b) Gill, G. B. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 3, p 887. (c) Regitz, M.; Maas, G. *Diazo Compounds*; Academic Press: New York; 1986. (d) Ando, W. In *The Chemistry of Diazonium and Diazogroups*; Patai, S., Ed.; John Wiley: Chichester, 1978; Part 1, p 458. (e) Meier, H.; Zeller, K. P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32. (f) Bachman, W. E.; Strove, W. S. *Org. React. (N.Y.)* **1942**, *1*, 38.

(2) (a) Matthews, J. L.; Braun, C.; Guibourdenche, C.; Overband, M.; Seebach, D. In *Enantioselective Synthesis of β-amino acids*; Juaristie, E., Ed.; Wiley-VCH: New York, 1996. (b) Sonawane, H. R.; Bellur, N. S.; Ahuja, J. R.; Kulkarni, D. G. *J. Org. Chem.* **1991**, *36*, 1431. (c) Sudrik, S. G.; Nanjundiah, B. S.; Sonawane, H. R. *Indian J Chem* **1997**, *36B*, 1103.

(3) Wilds, A. L.; Meader, A. L. *J. Org. Chem.* **1948**, *13*, 3.

(4) Vleggaar, J. J. M.; Huizer, A. H.; kraakman, P. A.; Nijssen, W. P. M.; Visser, R. J.; Verma, C. A. G. O. *J. Am. Chem. Soc.* **1994**, *116*, 11754.

(5) (a) Lee, V.; Newman, M. S. *Org. Synth. (N.Y.)* **1970**, *50*, 77. (b) Newman, M. S.; Beal, F. *J. Am. Chem. Soc.* **1950**, *72*, 5163. (c) Newman, M. S.; Arkell, A. *J. Org. Chem.* **1959**, *24*, 385.

(6) Maas, G. In *Houben-weyl Methodender Organischen Chemie, Carbene*; Regitz, M., Ed.; Theime: Stutgart, 1989; E19b, p 2.

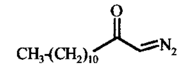
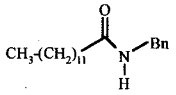
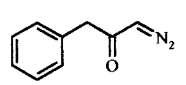
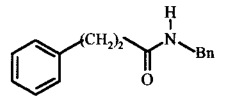
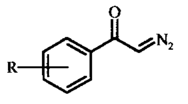
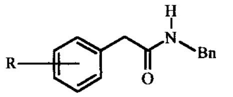
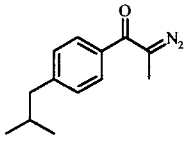
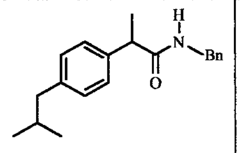
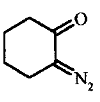
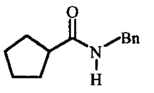
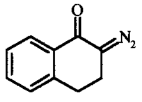
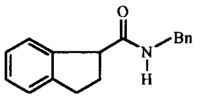
(7) Muller, A.; Vogt, C.; Sewald, N. *Synthesis* **1998**, 837.

(8) (a) Marquie, J.; Laporterie, A.; Duhac, J. *J. Org. Chem.* **2001**, *66*, 421. (b) Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathe, D. *Synthesis* **1998**, 1213. (c) Caddick, S. *Tetrahedron* **1995**, *51*, 10403. (d) Strauss, C. R.; Trainor, R. W. *Aust. J. Chem.* **1995**, *48*, 1665. (e) Gedye, R. N.; Rank, W.; Westaway, R. C. *Can J Chem.* **1991**, *69*, 706. (f) Abramovitch, R. A. *Org. Prep. Proc. Int.* **1991**, *23*, 683. (g) Larhed, M.; Hallberg, A. *J. Org. Chem.* **1996**, *23*, 683. (h) Gigure, R. J.; Bray, T. R.; Duncan, S. M. *Tetrahedron Lett.* **1986**, *27*, 4945.

(9) (a) Morcuende, A.; Ors, M.; Valverde, S.; Herradon, B. *J. Org. Chem.* **1996**, *61*, 5264. (b) Pagnotta, M.; Pooley, C. L. F.; Gurland, B.; Choi, M. *J Phys. Org. Chem.* **1993**, *6*, 407. (c) Deka, N.; Sarma, J. C. *J. Org. Chem.* **2001**, *66*, 1947.

10.1021/jo010951a CCC: $22.00

Table 1

Entry	α-Diazoketone	Benzylamide	Yield (%)		Dipole moments[a] (Debye)	
	1	**2**	Micro-wave[16]	Thermal[17]	Z[b]	E
(a)			75	45	3.69	1.89
(b)			92	56	3.42(3.31)	1.75
						
(c)	R = H	R = H	74	54	3.65(3.66)	1.78
(d)	R = 2-Me	R = 2-Me	93	52	3.3	1.82
(e)	R = 2-Cl	R = 2-Cl	68	48	4.1(3.56)	2.24
(f)	R = 2-Br	R = 2-Br	74	38	4.19	2.35
(g)	R = 2-I	R = 2-I	82	41	3.75	1.93
(h)	R = 4-Me	R = 4-Me	74	36	3.9(4.1)	2.5
(i)	R = 4-OMe	R = 4-OMe	87	74	4.75(3.62)	3.37
(j)			86	32	4.0	1.93
(k)			90	57	3.71	--
(l)			72	55	3.87	--

[a] indicates dipole moments of the starting materials α-diazoketones in *Z* and *E* forms (Figure 1) are calculated through PM3 method using HYPERCHEM software. [b] The values reported in the literature[11] are noted in the parentheses.

elegant account of the parameters responsible for the dielectric heating. The origin of the heating effect produced by the microwaves arise from the ability of an electric field to exert a force on charged particles. The net result of this interaction gives rise to dielectric polarization, which can be expressed by the Debye equation. The total polarization is the sum of electronic polarization, atomic polarization, dipolar polarization, and interfacial polarization. Among these the principal contributor to this is the dipolar polarization, resulting from the orientation of the dipoles by the electric field. In this context it may be noted that the substrates of the Wolff rearrangement contain the α-diazocarbonyl group capable of resonance as a characteristic structural unit (Figure 1). As a consequence they possess high permanent dipole moments[11] (Table 1) and render themselves microwave active. The vectorial analysis of these resonance conformers clearly shows that the *Z*-type resonance conformers **1a(i–iii)** (Figure 1) have higher dipole moments than the corresponding *E*-type conformers **1a(iv–vi)**. This aspect was further supported by theoretical calculations of dipole moments (Table 1 and Table 2) made using PM3 and ab initio calculations (vide infra). These results suggest that the *Z*-type configuration is the preferred orientation to align with the electric field of microwaves following coupling between dielectrics of a molecule and microwaves. Additionally, the judicious choice of solvent in terms of its microwave absorption capacity may allow one to observe the chemistry arising either from the direct interaction of the α-diazoketones with microwaves (nonthermal effect) or through solvent heating (thermal effect). Accordingly, we demonstrate

---

(10) (a) Mingos, D. M. P.; Baghurst, D. R. *Chem. Rev.* **1991**, *20*, 1. (b) Gabriel, C.; Gabriel, S.; Grant, E. H.; Halstead, B. S. J.; Mingos, D. M. P. *Chem. Soc. Rev.* **1998**, *27*, 213. (c) Galena, S. A. *Chem. Soc. Rev.* **1997**, *26*, 233.

(11) (a) Piazza, G.; Sorriso, S.; Foffani, A. *Tetrahedron* **1968**, *24*, 4751. (b) Sorriso, S.; Piazza, G.; Foffani, A. *J. Chem. Soc. B* **1971**, 805.- (c) Sorriso, S.; Foffani, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1497. (d) Sorriso, S.; Foffani, A. *J. Chem. Soc., Perkin Trans. 2* **1973**, 2142.

Table 2. Dipole Moment and Energy of the Endo (1mE) and Exo (1mZ) Conformers of 3-Diazocamphor[a]

	dipole moment[a]		energy[b]	
basis set	endo (**1mE**)	exo (**1mZ**)	endo (**1mE**)	exo (**1mZ**)
3-21G	3.9397	3.9565	−567.2162894	−567.2124763
3-21G(d,p)	3.7980	3.9130	−567.3791993	−567.3776416
3-21G++(d,p)	4.6353	4.7345	−567.4402857	−567.4392741
6-31G	4.4126	4.5283	−570.2245033	−570.2242355
6-31G(d,p)	3.8529	3.9429	−570.5171595	−570.5163425
6-31G++(d,p)	4.1220	4.2123	−570.5272696	−570.5265600

[a] In Debye units. [b] In Hartree units

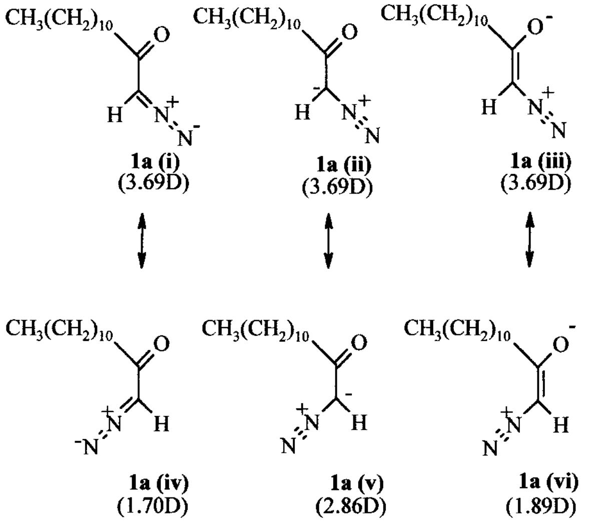


Figure 1.

gainful utilization of this feature in the microwave-promoted Wolff rearrangement, which occurs via the *Z*-conformation.[11,12] Additionally, a recent report[13] involving the utility of α-diazoketone to form β-lactams via ketene prompts us to report our findings in this area.

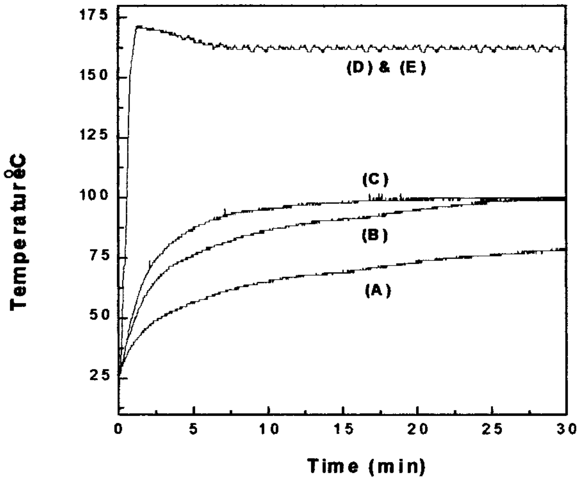


Figure 2. Temperature profile with respect to time during the microwave irradiation (300 W) of (A) anhydrous benzylamine, 10 mL; (B) a 0.1 M solution of α-diazoketone **1a** in benzylamine, 10 mL; (C) a 0.1 M solution of the 3-diazocamphor **1m** in benzylamine, 10 mL; (D) an aqueous dioxane solution (H_2O:dioxane, 1:1 vol/vol), 10 mL; and (E) 3-diazocamphor **1m** in aqueous dioxane (H_2O:dioxane, 1:1 vol/vol), 10 mL.

Results and Discussion

A variety of α-diazoketones **1a**−**m** are synthesized by following the literature procedures from either deformylative diazo transfer[14] or acylation of diazomethane.[15] The dilute solutions of these substrates in benzylamine[16] are subjected to the continuos mode of microwave irradiation[17] ($\nu = 2450$ MHz) with an irradiation power of 300 W. Additionally, for comparison purposes, these solutions are refluxed (∼170 °C) for 15 min using conventional heating techniques[18] and the results are summarized in Table 1. The progress of the microwave-promoted reaction was monitored by following the change in solution temperature and reactor pressure with respect to time (Figure 2 and Figure 3). The graph 2A (Figure 2) generated during the microwave irradiation of benzylamine at an irradiation power of 300 W shows the typical nature of microwave heating. The rate of heating is faster in the initial period of time and it decreases and eventually becomes constant with an increase in the length of time. A maximum solution temperature of 87 °C was reached after irradiating for 26 min. Irradiating with a more intense microwave (600 W) resulted in the initial acceleration of the rate of heating. However, a proportionate rise in the temperature was not observed. A maximum solution temperature of 97 °C is reached, indicating that there is a limit to temperature achieved under these conditions. The graph 2B (Figure 2) recorded during microwave irradiation with an intensity of 300 W of the dilute solution of α-diazoketone **1** in benzylamine also shows the typical features of dielectric heat-

---

(12) (a) Sorriso, S. In *The chemistry of Diazonium and Diazo groups*; Patai, S., Ed.; John Wiley: Chichester, 1978; Chapter 3. (b) Nikolaev, V. A.; Popik, V. V. *Tetrahedron Lett.* **1992**, *33*, 4483.

(13) Linder, M. R.; Podlech, J. *Org. Lett.* **2001**, *3*, 1849.

(14) Taber, D. F.; Runkle, R. E.; Hennessy, M. *J. Org. Chem.* **1986**, *51*, 4077.

(15) Bridson, J. N.; Hooz, J. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 386.

(16) A solvent/substrate with a high dipole moment, more correctly possessing a higher dielectric loss tangent, is beneficial for efficient absorption of microwave energy. Amines are known to couple less effectively with microwaves than alcohol, water, amides, nitriles, etc. (Gedye, R. N.; Smith, F. E.; Westaway, K. C. *Can. J. Chem.* **1988**, *66*, 17. see also ref 10).

(17) General Procedure: A solution of α-diazoketone **1a**−**m** in anhydrous benzylamine (0.1 M, 10 mL) is charged in a sealed Teflon reactor (100 mL) equipped with temperature and pressure sensors and subjected to the continuos mode of microwave irradiations ($\nu = 2450$ MHz) with irradiation power of either 300 or 600 W using a Microwave Assisted Reactor System-5 [MARS-5 (CEM Corpn., USA)] till the change in the reactor pressure becomes constant (∼15−30 min). The excess benzylamine is distilled off under reduced pressure and the residue chromatographed over silica gel using a petroleum ether:ethyl acetate gradient to obtain the Wolff-rearranged products **4a**−**m**. Recrystallization from aqueous ethanol furnished pure benzyl amides in excellent yields and the melting points are found to be in agreement with those reported in the literature.

(18) General procedure for the conventional thermolysis: A solution of α-diazoketones **1a**−**m** (1 mmol) in anhydrous benzylamine (5 mL) is added to the refluxing benzylamine (5 mL) over 5 min and refluxed. Infrared spectral analysis indicated the total disappearance of the starting α-diazoketones (∼10 min). The solvent is removed under reduced pressure and the residue chromatographed over silica gel using a petroleum ether:ethyl acetate gradient as eluent.

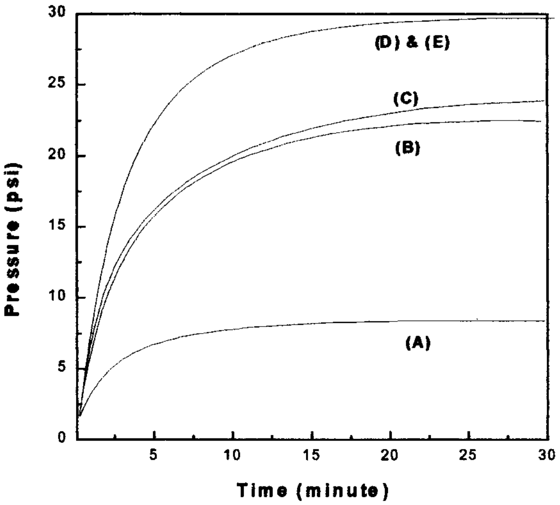
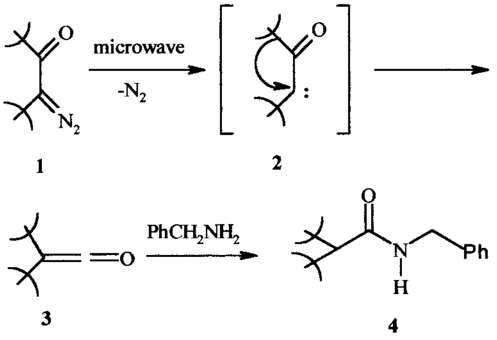


Figure 3. Pressure profile with respect to time during the microwave irradiation (300 W) of (A) anhydrous benzylamine, 10 mL; (B) a 0.1 M solution of α-diazoketone **1a** in benzylamine, 10 mL; (C) a 0.1 M solution of the 3-diazocamphor **1m** in benzylamine, 10 mL; (D) an aqueous dioxane solution (H_2O:dioxane, 1:1 vol/vol), 10 mL; and (E) 3-diazocamphor **1m** in aqueous dioxane (H_2O:dioxane, 1:1 vol/vol), 10 mL.

Scheme 1



ing; this graph is distinct from the graph 2A (Figure 2) in the aspect that a much higher solution temperature (99 °C) in a much smaller time (10 min) is achieved, thus revealing the more effective coupling of the microwaves with the α-diazoketones than with the benzylamine. The liberation of nitrogen gas during the course of the reaction (Scheme 1) was advantageously used in monitoring the completion of the decomposition of α-diazoketones. The microwave irradiation was continued till the change in reactor pressure became constant (∼25 min, Figure 3).

A wide range of α-diazoketones are subjected to microwave irradiation in benzylamine.[17,19] The results obtained thereof, summarized in Table 1, bring forth the superiority of microwave-promoted rearrangement over the conventional thermal reaction. Aliphatic (**1a**), benzylic (**1b**), and substituted aromatic (**1c**−**j**) α-diazoketones under the influence of microwaves gave excellent yields of the Wolff-rearranged benzyl amides; also the cyclic α-diazoketones (**1k**−**l**) underwent an efficient ring contraction reaction. It is remarkable to note[20] that the nonlinear α-diazoketone **1j** furnished exclusively the benzyl amide of ibuprofen, an important antiinflammatory agent.[21] The efficiency and simplicity of this protocol can be profitably utilized in combinatorial chemistry.[22]

Encouraged by the results obtained from the conformationally mobile α-diazoketones, we chose a conformationally restricted substrate such as 3-diazocamphor **1m** known for its distinct and diverse thermal and photochemical behavior[1e] to probe the hotly debated issue of specific microwave effect or nonthermal effect.[8−10] The substrate **1m** on thermolysis[23] or on transition metal catalysis[24] is known to undergo intramolecular C−H insertion to give tricyclic ketone **5**. Photolysis[25] in methanol yields the methyl ester of the Wolff rearrangement product **6** (Scheme 2).

We performed the molecular orbital calculations to predict the thermodynamic stability and the dipole moment of the endo **(1mE)** and exo **(1mZ)** resonance conformers of 3-diazocamphor **1m** (Figure 4). The geometries were optimized with the use of split-valence basis sets, 3-21G, 3-21G(d,p), 6-31G, and 6-31G(d,p) without any symmetry constraints. We have also performed the stationary point energy calculation using the polarization and diffusion functions on the structures optimized at the level of 3-21G(d,p) and 6-31G(d,p). All the ab initio calculations were performed using the GAMESS program[26] and the initial geometries were generated using the MOLDEN software.[27] The energy and dipole moments of the endo **(1mE)** and exo **(1mZ)** conformers of the 3-diazocamphor are given in Table 2. It is seen that the thermodynamic stability of the endo **(1mE)** conformer is greater than the exo **(1mZ)** conformer whereas the dipole moment order is seen to be reversed. The usage of polarization and the diffuse functions actually improves the difference in the value of the dipole moment of endo and exo conformers, significantly. However, the predicted energy difference values for both conformers are slightly reduced with the use of polarization or diffuse functions. In all cases, one can see the that dipole moment of the *Z*-conformer is higher than that of the *E*-conformer and the latter conformer is thermodynamically more stable[28] than that of the former conformer.

---

(19) The control experiment: A solution of the α-diazoketone **1a** in anhydrous benzylamine (0.1 M, 10 mL) is heated using an oil bath around 100 °C for 20 min. The infrared analysis of the solution revealed the presence of the starting α-diazoketone. This was further confirmed from the near quantitative recovery of **1a** after standard workup.

(20) The silver(I) oxide catalysis of the α-diazopropiophenone gives a mixture of the Wolff rearrangement product ketene and *β*-hydride elimination product enone in the ratio of 44:56, respectively. This ratio is on the same order as the ratio of *Z*- and *E*-resonance conformers. Franzen, V. *Chem. Ber.* **1957**, *602*, 199; see also refs 5c and 12a.

(21) Sonawane, H. R.; Nanjundiah, B. S.; Ahuja, J. R.; Kulkarni, D. G. *Tetrahedron: Asymmetry* **1992**, *3*, 163.

(22) (a) Hermkens, P. H. H.; Ottenheijm, H. C. J.; Rees, D. *Tetrahedron* **1996**, *52*, 4527. (b) Fruchtel, J. S.; Jung, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 17.

(23) Horner, L.; Spietschka, E. *Chem. Ber.* **1955**, *88*, 934.

(24) Brown, F. C.; Morris, D. G.; Murray, A. M. *Synth. Commun.* **1975**, *5*, 477.

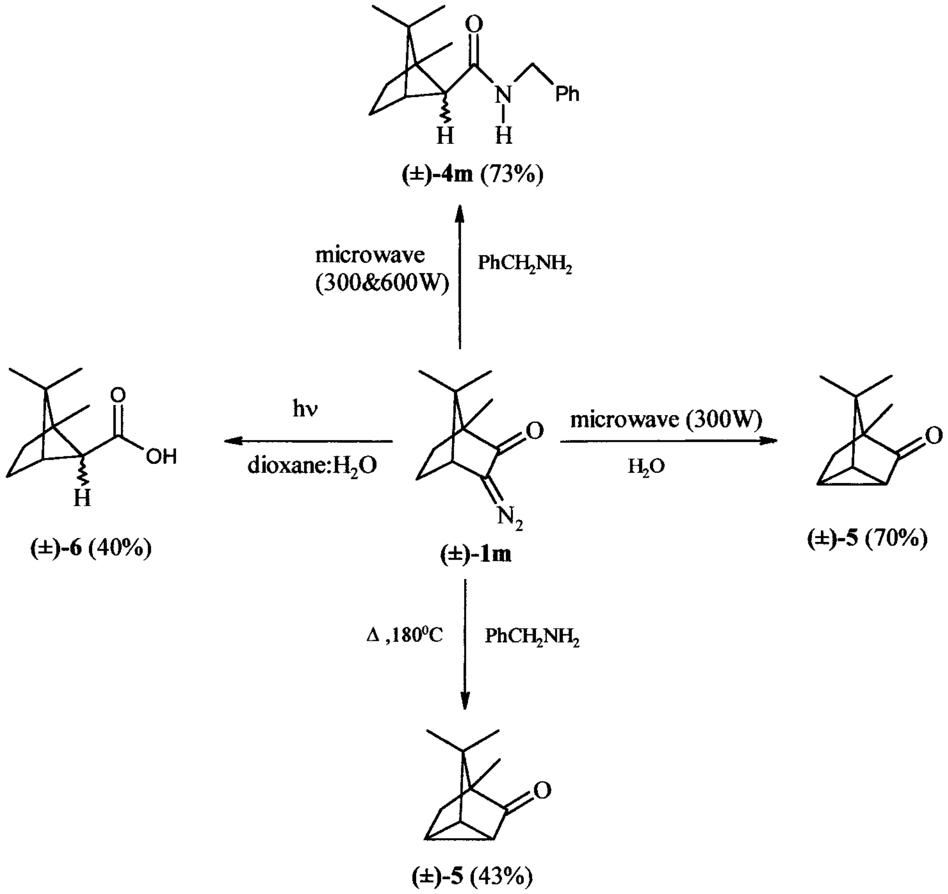
(25) (a) Rau, H.; Bokel, M. *J. Photochem. Photobiol. A* **1990**, *53*, 311. (b) Becker, E.; Weiland, R.; Rau, H. *J. Photochem. Photobiol. A* **1988**, *41*, 330.

(26) Schmidt, M. W.; Baldridge, K. K.; Boatx, J. A.; Elbert, S. T.; Gordan, M. S.; Jensen, J. S.; Koseki, S.; Matsunga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, S.; Montgomery, J. A. *J. Comput. Chem.* **1992**, *14*, 1347.

(27) (a) Schaftenaar, G. CAOS/CAMM, Center Nijmegen, Toernooived, Nijmegen, The Netherlands, 1991. (b) http://www.cmbi.kun.nl/∼schaft/molden.html.

(28) It is interesting to note that the UV−visible spectral analysis of 3-diazocamphor shows that the carbonyl and diazo chromophores overlap to a smaller extent compared to aliphatic α-diazoketones, suggesting the predominant existence of the thermodynamically more stable **1m(*E*)** conformer. (a) Weiland, B. R.; Rau, H. *J. Photochem. Photobiol. A* **1988**, *41*, 330. (b) Rau, H.; Bakel, M. J. *J. Photochem. Photobiol. A* **1990**, *53*, 311.

Scheme 2



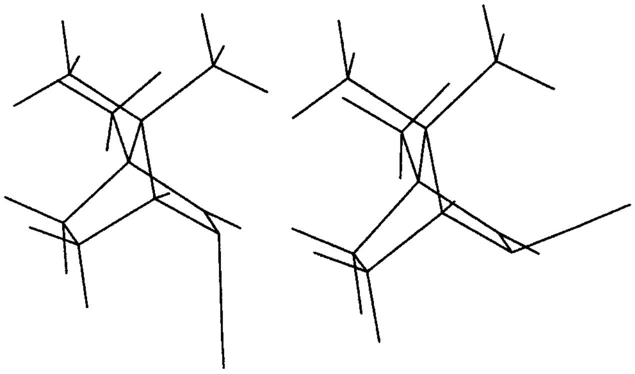


Figure 4.

Thus it is observed that the difference of dipole moments of endo **(1mE)** and exo **(1mZ)** conformers is supported by ab initio calculations with a sufficiently large basis set.

With this background we expected 3-diazocamphor **1m** to undergo Wolff rearrangement on microwave irradiation, in sharp contrast to its known thermal behavior and, indeed, this was found to be the case (Scheme 2). Microwave irradiation of a solution of **1m** in benzylamine with the irradiation power of 300 W, graph 2C (Figure 2), gave exclusively a diastereomeric mixture (45:55) of the ring-contracted bicyclic benzyl amide **4m** in 73% yield. The transformation was complete in nearly 30 min. A microwave irradiation at higher irradiation power (600 W) was carried out in consideration of the three aspects: (i) randomly oriented molecules possessing weaker dipole moments are forced to orient with the electric field of the microwaves, (ii) relaxation time of the metastable state is increased, and (iii) acceleration in the rate of reaction. Here too, the Wolff rearrangement product **4m** is formed exclusively in a much shorter reaction time (~18 min). In comparison, refluxing a solution of α-diazoketone **1m** in benzylamine for 15 min furnished product **5** (43%) arising from the intramolecular C−H insertion.[22] Exposing an aqueous dioxane solution of α-diazoketone **1m** to ultraviolet light ($\lambda \sim 300$ nm) for 3 h yielded a diastereomeric mixture (85:15) of the ring-contracted carboxylic acid (±)-**6** in 40% yield.

We attribute this microwave-specific behavior exhibited by 3-diazocamphor (Scheme 2) to the effective coupling of dielectrics of the α-diazoketone **1m** with microwaves followed by orientation of resonance conformer (**1mZ**) possessing a higher electric dipole moment accompanied by its alignment with the electric field of the microwaves leading to the formation of observed product **4m**. A similar mechanism may be operating in other conformationally mobile α-diazoketones **1a**−**l** as can be judged from the enhanced yields of the rearrangement products **2a**−**l**, as well as from the formation of the sole product namely benzyl amide of ibuprofen (**4j**) from the nonlinear α-diazoketone (**1j**). In a nutshell, it appears that in conventional thermolysis reaction occurs predominantly through the thermodynamically more stable conformer, while the conformer possessing the highest dipole moment is preferred in the microwave irradiation.

In converse to the above work, we conducted a microwave irradiation (300 W) of 3-diazocamphor in the presence of water having comparatively much higher microwave absorption ability (dielectric loss tangent = 0.123 at $\nu = 2450$ MHz). A sharp increase in the rate of heating was noticed with a consequent rise in the solution temperature to 170 °C (Figure 2, graph 2E). The perfectly superimposable nature of graphs 2D and 2E testifies that the water is a superior microwave absorber than the α-diazoketone **1m**. The reaction was complete within minutes of the irradiation (Figure 3, graph 3E). The product analysis revealed the formation of tricyclic ketone **5** as the principal product along with several side products. This result falls in line with the results obtained by refluxing the solution of **1m** in benzylamine, strongly suggesting the occurrence of a through solvent heating process.[23,29]

Conclusion

In conclusion, we have demonstrated that microwave irradiation of the α-diazoketones promotes efficient Wolff rearrangement of tremendous synthetic utility and the product selectivity depends on the dielectric properties of the solvent used. Formation of the ring-contracted bicyclic amide, a nonthermal reaction product from 3-diazocamphor most probably due to the combined solvent and microwave effect, gives impetus to further studies in this direction.

Acknowledgment. S.G.S., S.P.C., andK.R.S.C. thank CSIR New Delhi, India for the award of research fellowships. We are also thankful to Dr. H. S. Potdar and Mr. Y. B. Kollam for their help in carrying out microwave experiments.

Supporting Information Available: Spectral data table of compounds **1a**−**l**, **2a**−**l**, **1m**, **4m**, **5**, and **6**. ^{1}H NMR, ^{13}C NMR, MS of **2j**, **1m**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010951A

---

[29] The conventional thermolysis of 3-diazocamphor gave the same tricyclic ketone arising from the intramolecular C−H insertion reaction irrespective of the solvent used (aniline, benzyl alcohol, *N*,*N*-dimethylaniline, etc.).