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Laser drop and low intensity photolysis of 2-diazo-1,3-indandione: evidence for a propadienone intermediate

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Abstract

Formation of diester **7** during laser drop photolysis of diazoindanone **1** is proposed to involve the intermediacy of propadienone **9** formed by high intensity photodecomposition of ketene **2**.

Keywords: Laser drop photolysis; Low intensity photolysis; Propadienone

1. Introduction

The phototransformation of α-diazo ketones into ketenes involves the 1,2 migration of a carbon atom, known as the Wolff rearrangement. Ketenes generated by the photolysis of α-diazo ketones can be trapped by nucleophiles at the oxy-substituted carbon to form detectable acid enols which undergo tautomerization to the corresponding acid or acid derivative [1,2].

In the case of cyclic α-diazoketones, the Wolff rearrangement leads to ring contraction and is a useful method for the synthesis of benzocyclobutenes from diazoindanones [3,4]. Cava and coworkers [5,6] reported that the gas phase pyrolysis (680 °C) of 2-diazo-1,3-indandione (**1**) in the presence of methanol gave satisfactory yields of the corresponding benzocyclobutenone-2-carboxylic acid methyl ester, **4** (Scheme 1).

The photolysis of **1** in methanol gave the diester of homophthalic acid (**7**) together with lesser amounts of 1,3-indandione and 3-methoxyisocoumarin. Cava and coworkers proposed [5,6] that **4** was formed but that further photolysis of this compound resulted in its conversion to **7** (Scheme 2).

The recently developed laser drop technique allows the preparation of small amounts of products from multiple-photon reactions [7]. In this technique small droplets of solution containing the substrate are excited by the focused beam from a pulsed laser. Because of the high photon flux, transient intermediates with suitable absorption properties may absorb a second (or third) photon if they are produced within the duration of the laser pulse [7,8]. This technique can only lead to secondary photoproducts resulting from further photolysis at the irradiating wavelength if those products are formed very rapidly, otherwise their formation would only take place once the irradiation, by the short laser pulse, is complete.

We recently reported that ketene **2** has a lifetime of 140 ns in methanol and decays to give the enol ester **3** which has a lifetime of 56 μs [9]. We reasoned that the photochemical preparation of the esters **4** should be possible under laser drop conditions without the formation of the diesters **7**, since **4** would not have formed to any significant extent (less than 4%) within the duration of the laser pulse. In this preliminary communication we report the results of these experiments.

2. Results and discussion

Lamp irradiation of a 1.0 mM deaerated solution of **1** in methanol at 300 nm for 5 min results in approximately 40% conversion to **4** and **7** in a 5-to-4 ratio as determined by gas chromatography; no other products were found. Prolonged irradiation results in a decrease in this ratio. Irradiations in isopropanol resulted in a similar ratio for the corresponding ester and diester products when the conversion was up to 40%; however, the major product is 1,3-indandione which accounted for 47% of the products formed at low conversions; it is probably formed via reductive radical processes involving the ketyl radical from 2-propanol. Prolonged irradiation resulted in a complex mixture of products which were not identified.

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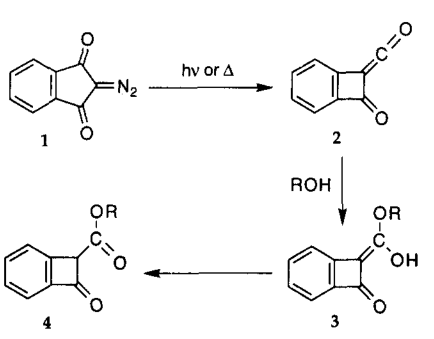
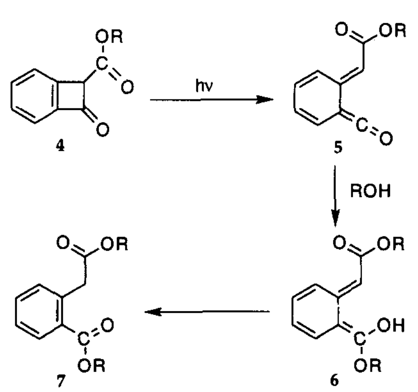


Scheme 1.

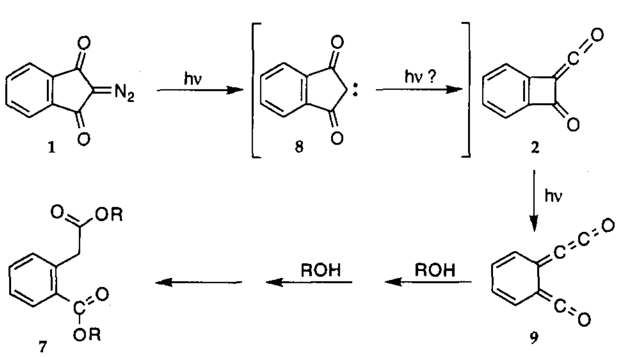


Scheme 2.

Table 1
Power dependence of the 7:4 product ratio following laser drop photolysis

Laser power [a] (%)	7:4 ratio
≤25	≈0
49	0.03
72	0.50
100	1.25

[a] 100% power corresponds to ca. 100 mJ pulse^{-1}.



Scheme 3.

When 0.20 mM solutions of **1** in methanol were subjected to 308 nm laser drop photolysis (about 100 mJ pulse^{-1}, one cycle) the conversion was 20% and only the monoester and the diester (**4** and **7**) were formed in a 4-to-5 ratio. The power dependence of the product ratio was examined by attenuating the laser with calibrated neutral density filters during laser drop photolysis: it was found that the **7**:**4** ratio increased dramatically with increasing laser power, as illustrated in Table 1. Interestingly, the products are free of **7** only when relatively low intensity irradiation is combined with the temporal characteristics of the laser drop technique.

Laser flash photolysis of **1** in methanol shows that neither the ester **4** nor its enol tautomer **3** is formed within the duration of the laser pulse [9]. Thus we expected that **7** would not be formed during laser drop photolysis if its formation involved the mechanism of Scheme 2. However, this product was formed in substantial amounts as was the corresponding diester in isopropanol. The power dependence on the product ratio during laser drop photolysis (Table 1) indicates that **7** is formed by a multiple-photon reaction. The photolysis of benzocyclobutenones is known to give ring-opened *o*-xylylene type intermediates [10,11] and the photoinduced ring opening of **4** is sufficiently facile that the low-intensity photolysis of **1** in alcohols gives substantial amounts of the diester even at low conversions of starting material. However, under laser drop conditions, photolysis of **4** is not possible. We propose that ketene **2** may absorb a second (or third) photon resulting in the formation of the propadienone **9**; this species can then be trapped by two molecules of alcohol in a stepwise process to form the diester **7** (Scheme 3), thus providing an alternate high intensity route to **7**.

Previous studies have shown that the electronic excitation of α-ketocarbenes results in a photoinduced Wolff rearrangement to form the corresponding ketene (*vide supra*) [12–14]. We cannot determine from these experiments whether or not the carbene **8** [15] is involved in the multiple-photon reaction which results in the formation of the diester **7**. Ketene **2**, formed within the duration of the laser pulse, provides a clear route to **7** via the intermediacy of **9**.

Simple propadienones have been extensively studied by flash vacuum pyrolysis of 5-alkylidene-1,3-dioxan-4,6-diones [16–18]. Propadienones could be easily trapped by alcohols to form the corresponding acrylic acid esters. A later study by Wentrup and Lorencak [19] unraveled the mechanism which leads to their formation and also found that propadienones are remarkably stable in the gas phase, requiring temperatures as high as 800 °C before they isomerize to vinyl ketenes.

It is unlikely that the low intensity photolysis of **1** in alcohols proceeds through the same mechanism as that of laser drop photolysis. This is because the intermediate ketene is too short-lived in methanol (about 140 ns) to absorb a second photon under low intensity conditions and has a much smaller extinction coefficient at the wavelengths used for low intensity irradiation (275–325 nm). Thus, the low intensity irradiation of **1** must proceed through the simple mechanism shown in Schemes 1 and 2.

3. Conclusion

Laser flash photolysis combined with laser drop photolysis has shown that the mechanism of conversion of 2-diazo-1,3-

indandione (**1**) in alcohols to form the diester of homophthalic acid is dependent on the intensity of the irradiation source. At low intensities the process is mediated by secondary photolysis of the product, **4**. In contrast, laser drop photolysis decomposition occurs in a multiphoton fashion involving photolysis of the intermediate ketene (**2**), leading indirectly to evidence for the intermediacy of **9**.

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References

[1] T. Shibata, K. Koseki, T. Yamaoka, M. Yoshizawa, H. Uchiki and T. Kobayashi, *J. Phys. Chem.*, *92* (1988) 6269.

[2] B. Urwyler and J. Wirz, *Angew. Chem.*, *Int. Edn. Engl.*, *29* (1990) 790.

[3] M.P. Cava, R.L. Litle and D.R. Napier, *J. Am. Chem. Soc.*, *80* (1958) 2257.

[4] I.L. Klundt, *Chem. Rev.*, *70* (1970) 471.

[5] M.P. Cava and R.J. Spangler, *J. Am. Chem. Soc.*, *89* (1967) 4450.

[6] R.J. Spangler, J.H. Kim and M.P. Cava, *J. Org. Chem.*, *42* (1977) 1697.

[7] J.T. Banks and J.C. Scaiano, *J. Am. Chem. Soc.*, *115* (1993) 6409.

[8] J.T. Banks and J.C. Scaiano, *J. Phys. Chem.*, *99* (1995) 3527.

[9] N. Camara de Lucas, J. Andraos, J.C. Netto-Ferreira and J.C. Scaiano, *Tetrahedron Lett.*, *36* (1995) 677.

[10] R. Boch, J.C. Bradley, T. Durst and J.C. Scaiano, *Tetrahedron Lett.*, *35* (1994) 19.

[11] D.R. Boate, L.J. Johnston, P.C. Kwong, E. Lee-Ruff and J.C. Scaiano, *J. Am. Chem. Soc.*, *112* (1990) 8858.

[12] R.A. Hayes, T.C. Hess, R.J. McMahon and O.L. Chapman, *J. Am. Chem. Soc.*, *105* (1983) 7787.

[13] R.J. McMahon, O.L. Chapman, R.A. Hayes, T.C. Hess and H.P. Krimmer, *J. Am. Chem. Soc.*, *107* (1985) 7597.

[14] S. Murata, T. Yamamoto and H. Tomioka, *J. Am. Chem. Soc.*, *115* (1993) 4013.

[15] J.J.M. Vleggaar, A.H. Huizer, P.A. Kraakman, W.P.M. Nijssen, R.J. Visser and C.A.G.O. Varma, *J. Am. Chem. Soc.*, *116* (1994) 11754.

[16] R.F.C. Brown and G.L. McMullen, *Aust. J. Chem.*, *27* (1974) 2385.

[17] R.F.C. Brown, F.W. Eastwood and K.J. Harrington, *Aust. J. Chem.*, *27* (1974) 2373.

[18] R.F.C. Brown, F.W. Eastwood and G.L. McMullen, *J. Am. Chem. Soc.*, *98* (1976) 7421.

[19] C. Wentrup and P. Lorencak, *J. Am. Chem. Soc.*, *110* (1988) 1880.