

## Reversible Photochemical Valence Isomerization between $\alpha$ -Diazo-ketones and $\alpha$ -Keto-diazirines<sup>1</sup>

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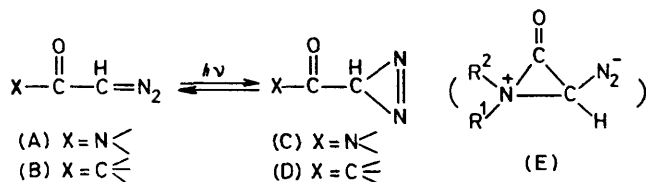
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**Summary** The photochemically induced valence isomerization of  $\alpha$ -diazocarbonyl compounds to give diazirines which had previously been pointed out to be restricted to  $\alpha$ -diazo-amides has now been observed in the  $\alpha$ -diazoketones (**1**) and (**5**).

FRANICH, LOWE, and PARKER<sup>2</sup> have stressed that the photochemical isomerization of  $\alpha$ -diazocarbonyl compounds to

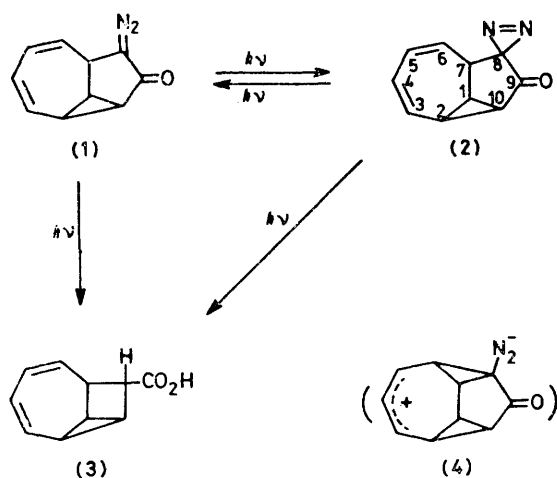
give diazirines is restricted to  $\alpha$ -diazo-amides (A), the excited state of which can be stabilized by the amide group in the canonical structure (E). Such isomerizations have apparently been reported only for certain linear<sup>2</sup> and cyclic<sup>3</sup>  $\alpha$ -diazo-amides; surprisingly the isomerization of  $\alpha$ -diazoketones (B) is not well known, even though many photo-induced Wolff rearrangements<sup>4</sup> of  $\alpha$ -diazoketones (B) have been reported. We now report the first observation of the

reversible photochemical valence isomerization between (B) and (D).

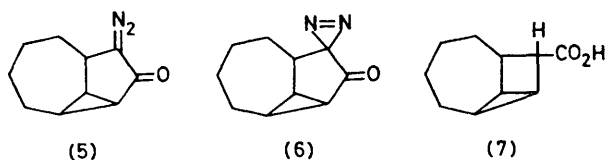


When a solution of 8-diazotricyclo[5.3.0.0<sup>2,10</sup>]deca-3,5-dien-9-one (1) (m.p. 50 °C; orange needles)<sup>†</sup> in aqueous dioxan was irradiated (>290 nm) for 3 h, the *endo*-carboxylic acid (3) (m.p. 166 °C; 42.5%)<sup>‡</sup> and the isomeric compound (2) (m.p. 65 °C; needles, 16%)<sup>‡</sup> were isolated together with recovered (1) (11.4%). The structure of (2) was unequivocally determined by its spectral properties. In particular, the 6-H n.m.r. absorption at  $\delta$  5.48, at high field relative to the other olefinic hydrogens, proves the presence of the diazirine ring, which has a large diamagnetic anisotropy.<sup>7</sup> The  $\alpha$ -keto-diazirine (2) was found to be unexpectedly stable compared with 1-oxospiro[cyclohexane-2,3'-diazirine]<sup>8</sup> which is reported to decompose even at room temperature. Control experiments showed that the yield of (2) from (1) was less than 15–17% and that amounts of both (1) and (2), upon prolonged irradiation, gradually diminished with an increase in the yield of (3). Similar results were obtained in the irradiation of (2), which gave (1) and (3) under the same conditions. The yield of (1) from (2), similarly, was less than 12–13%. These observations indicate that the diazo-ketone-diazirine interconversion is photo-reversible and the Wolff rearrangement takes place from both (1) and (2) with slightly different rates.

In order to investigate the possibility that  $\pi$ -bond participation might stabilize an excited state of (1) in the canonical form (4), the saturated  $\alpha$ -diazoketone (5) (m.p. 49 °C)<sup>§</sup> was synthesized and irradiated under the same conditions. Careful examination of the photolysate showed



that a similar valence isomerization as observed for (1) had occurred. Thus, the  $\alpha$ -keto-diazirine (6) was isolated in 10.6% yield by t.l.c. (silica gel) together with the carboxylic acid (7).



The finding that both unsaturated and saturated  $\alpha$ -diazoketones (1) and (5) undergo valence isomerization to give the  $\alpha$ -keto-diazirines (2) and (6) suggests that the thermal and photochemical lability of  $\alpha$ -keto-diazirines, rather than a hypothetical stabilization effect such as the amide effect<sup>2</sup> or  $\pi$ -bond participation, is responsible for detection of the occurrence of valence isomerization for  $\alpha$ -diazocarbonyl compounds.

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<sup>†</sup> The diazo-ketone (1) was prepared by the procedure reported previously (ref. 5) starting from tricyclo[5.3.0.0<sup>2,10</sup>]deca-3,5-dien-9-one (ref. 6). Satisfactory elemental analyses were obtained for all new compounds. (1):  $\nu_{\text{max}}$  (KBr) 2080 and 1660  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (EtOH) 248.5 ( $\epsilon$ , 12,300), 300 (3686), and 392sh (37) nm;  $m/e$  (25 eV; 80 °C) 144, 116, and 115 (100%) ( $M^+$  not observed); n.m.r.  $\delta$  ( $\text{CDCl}_3$ ) 1.76 (dd, 10-H), 2.02 (ddd,  $J_{2,3}$  3.0,  $J_{2,10}$  10.5 Hz, 2-H), 2.37 (ddd,  $J_{1,10}$  5.0,  $J_{1,7}$  6.0,  $J_{1,2}$  7.0 Hz, 1-H), 4.32 (dd,  $J_{6,7}$  8.0 Hz, 7-H), and 5.80–6.40 (m, 3-, 4-, 5-, and 6-H).

<sup>‡</sup> (2):  $\nu_{\text{max}}$  (KBr) 1630 and 1720  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (EtOH) 253 ( $\epsilon$  41,600), 315 (180), and 330 (100) nm;  $m/e$  (25 eV; 80 °C) 172 ( $M^+$ , 2.3%), 144, 116, and 115 (100%); n.m.r.  $\delta$  ( $\text{CDCl}_3$ ) 2.03 (dd,  $J_{1,10}$  5.0 Hz, 10-H), 2.33 (dddd,  $J_{2,3}$  3.0,  $J_{2,10}$  10.0,  $J_{2,7}$  1.0,  $J_{2,4}$  1.0 Hz, 2-H), 2.82 (dddd,  $J_{1,6}$  0.5,  $J_{1,7}$  6.0,  $J_{1,2}$  7.0 Hz, 1-H), 3.18 (dddd,  $J_{5,7}$  0.6 Hz, 7-H), 5.48 (dddd,  $J_{6,8}$  11.5,  $J_{6,7}$  7.5,  $J_{4,6}$  1.5 Hz, 6-H), and 5.91–6.25 (m, 3-, 4-, and 5-H).

<sup>§</sup> The saturated  $\alpha$ -diazoketone (5) was prepared by the procedure reported previously (ref. 5) starting from tricyclo[5.3.0.0<sup>2,10</sup>]decan-9-one (ref. 6).

<sup>1</sup> For Part XL of the Series 'Organic Photochemistry,' see H. Saiki, T. Miyashi, T. Mukai, and Y. Ikegami, *Tetrahedron Letters*, 1977, 4619.

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