Photochemical Isomerisation of Some Diazo-compounds into Diazirines

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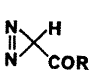
Summary The isomerisation of some diazo-acetamides into diazirinyl-amides has been effected with visible light.

DURING our investigations of the photochemistry of α-diazo-amides,[1] a study of the effect of wavelength revealed that irradiation of diazo-acetamides with visible light gave the isomeric diazirinyl-amides in about 20% isolated yield.

$N_2CR^2{\cdot}COR^1$

(1)



(2)

For example, N-diazoacetylpiperidine (**1**; $R^1 = C_5H_{10}N$, $R^2 = H$), prepared from N-glycylpiperidine by treatment with nitrous acid, gave on irradiation with visible light for 1 h, the N-diazirinylcarbonylpiperidine (**2**; $R = C_5H_{10}N$), ν_{max} (CCl_4) 1655 cm^{-1} (amide); λ_{max} (CCl_4) 303—312 (ϵ 130); τ (CCl_4) 8·18 p.p.m. (1H, s, diazirine H), whereas irradiation with u.v. light gave 1-azabicyclo[4,2,0]octan-8-one.[2] Irradiation of N-diazoacetyl-L-proline benzyl ester (**1**; R^1 = Pro·OBzl, $R^2 = H$) (Bzl = benzyl) and N-diazoacetyl-L-phenylalanine methyl ester (**1**; R^1 = Phe·OMe, $R^2 = H$),[3] also prepared by treatment of the corresponding N-glycyl-derivatives with nitrous acid, gave upon irradiation with visible light N-diazirinylcarbonyl-L-proline benzyl ester (**2**; R = Pro·OBzl), m.p. 98—100°, $[\alpha]_D^{20}$ $-94{\cdot}0$; m/e 273, $C_{14}H_{15}N_3O_3 = 273$; ν_{max} ($CHCl_3$) 1658 cm^{-1} (amide); λ_{max} (EtOH) 310 nm (ϵ 124); τ ($CDCl_3$) 8·17 p.p.m. (1H, s, diazirine H), and N-diazirinylcarbonyl-L-phenylalanine methyl ester (**2**; R = Phe·OMe), m.p. 104—105°, m/e 247, $C_{14}H_{15}N_3O_3 = 247$; λ_{max} (EtOH) 310 nm (ϵ 120); τ ($CDCl_3$) 8·40 p.p.m. (1H, s, diazirine H) respectively.

Irradiation of N-(t-butoxycarbonyldiazoacetyl)piperidine (**1**; $R^1 = C_5H_{10}N$, $R^2 = CO_2Bu^t$) and N-(t-butoxycarbonyldiazoacetyl)-L-proline benzyl ester (**1**; R^1 = Pro·OBzl, $R^2 = CO_2Bu^t$) with visible light however, did not generate the corresponding N-diazirinylcarbonyl-derivatives. It may be that the disubstituted diazirines are less stable or possibly revert to the corresponding diazo-compound. Diphenyldiazirine is considered to isomerise spontaneously to the diazo-compound owing to the steric repulsion between the substituents which is less severe in the diazo-compound.[4]

The diazirines gave good elemental analyses and contained the characteristic irregular u.v. absorption maximum at *ca.* 310 nm (ϵ *ca.* 120).[5,6] The n.m.r. spectra were virtually identical with those of the corresponding diazo-compounds except that the sharp one-proton singlet near τ 5 in the latter moved to τ *ca* 8·2 in the diazirines The remarkably high field required to bring this proton into resonance can be ascribed to the large diamagnetic anisotropy associated with the strained diazirine ring [6,7]

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