Indolo[6,7-*g*]indoles; a New Heteroaromatic System

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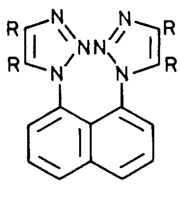
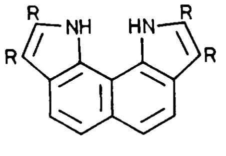
Photolysis of 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazoles in methanol has given the new heteroaromatic system compounds, indolo[6,7-*g*]indoles.

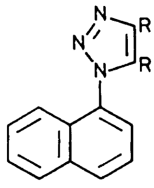
In connection with our study of the structure and reactivity of *peri*-substituted naphthalenes, we have synthesized novel 1,8-diheteroaromatic naphthalenes, 1,1′-(1,8-naphthylene)di-1*H*-1,2,3-triazoles (**1**), the structures of which have been studied by several spectral analyses.[1] According to the *X*-ray diffraction study, the naphthalene framework is very distorted owing to steric repulsion between the two triazole rings in these compounds.[2] We now report that photolysis of these compounds gives the novel heteroaromatic ring systems, indolo[6,7-*g*]indoles.



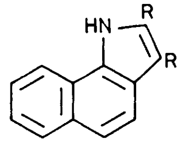
(1)



(2)



(3)



(4)

a; R = CO_2Et
b; R = CO_2Pr^i

Irradiation† of (**1a**) in methanol for 15 min afforded tetraethyl 1*H*,10*H*-indolo[6,7-*g*]indole-2,3,8,9-tetracarboxylate (**2a**) (70% yield),‡ which was produced by the elimination of N_2 from both triazole rings and cyclization. There are several kinds of indoloindole structures depending on the mode of condensation of the two indole rings, including indolo[3,2-*b*]indole[3] and indolo[7,6-*g*]indole.[4] However, to our knowledge, the indolo[6,7-*g*]indole skeleton has not previously been synthesised. The isopropoxycarbonyl derivatives (**2b**) were also produced by similar photolysis from (**1b**) in excellent yield.

A similar reaction is observed on photolysis of the corresponding monotriazoles (**3**). Irradiation of (**3a**) for 15 min in methanol gave diethyl 1*H*-benz[*g*]indole-2,3-dicarboxylate (**4a**) (95% yield). The formation of keteneimine and 1*H*-azirene derivatives, which were generated by the photolysis of 1,4,5-triphenyl-1,2,3-triazole[5] and 1,5-dimethyl-4-phenyl-1,2,3-triazole,[6] respectively, was not detected under these conditions.

In the ^1H n.m.r. spectrum, the NH signal of (**2a**) is *ca.* 0.9 p.p.m. downfield of that of (**4a**). This low field shift may be explained by the anisotropic effect between the two condensed indole rings. In the i.r. spectrum, the N–H stretching frequency of (**2a**) is about 100 cm^{-1} lower than that for (**4a**), which suggests the existence of strong intramolecular hydrogen bonding in (**2a**). Owing to the enlargement of the condensed ring, the longest wavelength band of (**2a**) shows about 30 nm red shift relative to that of (**4a**) in the u.v. spectrum.

Photolysis of (**1**) and (**3**) was followed by h.p.l.c. using an octadecylsilane column and MeOH–H_2O (90:10) as eluent. The starting material (**3a**) disappeared completely after 2 min irradiation, while (**1a**) required for 10 min irradiation before complete decomposition occurred. A similar difference in reactivity was observed between (**1b**) and (**3b**), indicating that monosubstituted naphthalenes (**3**) decompose much faster than disubstituted naphthalenes (**1**). The lower reactivity in (**1**) is probably caused by the proximity of the extra triazole ring perpendicular to the naphthalene ring, which inhibits the cyclization.

Received, 26th February 1988; Com. 8/00755A

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† Photolyses were conducted at ambient temperature using a 450 W USIO high pressure Hg lamp through a quartz well.

‡ All new compounds gave satisfactory elemental and spectroscopic analyses. Compound (**2a**), m.p.209—210 °C; u.v. (MeOH, 0.03 mM): $\lambda_{max.}$ 375.5, 361.3, 278.3, 246.9, 207.7 nm; i.r. (CCl_4, 2 mM): $\nu_{max.}$ 3351, 1730, 1698 cm^{-1}; ^1H n.m.r. ($CDCl_3$, 20 mM): δ (rel. Me_4Si) 1.45 (6H, t), 1.48 (6H, t), 4.48 (4H, q), 4.50 (4H, q), 7.68 (2H, d), 8.00 (2H, d), 11.44 (2H, s).

Compound (**4a**), m.p. 134—135 °C; u.v. (MeOH, 0.03 mM): $\lambda_{max.}$ 348.7, 335.3, 274.9, 248.5, 206.9 nm; i.r. (CCl_4, 2 mM): $\nu_{max.}$ 3448, 1732, 1697 cm^{-1}; ^1H n.m.r. ($CDCl_3$, 20 mM): δ (rel. Me_4Si) 1.43 (3H, t), 1.47 (3H, t), 4.47 (2H, q), 4.49 (2H, q), 7.51—7.61 (3H, m), 7.91 (1H, dd), 7.99 (1H, d), 8.23 (1H, d), 10.52 (1H, s).