A Novel Photochemical Ring Contraction of 4*H*-Pyrans. A New Route to Selectively Substituted Cyclobutenes

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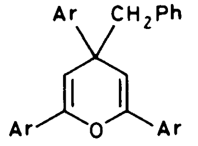
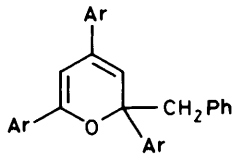
The novel photochemical ring contraction of some 4*H*-pyrans to cyclobutenes is described.

Previous studies on the photochemical behaviour of 4*H*-pyrans have identified two modes of reactivity: (i) 1,3-benzyl migration in the triaryl substituted derivatives (**1**) to afford the 2*H*-isomers (**2**)[1] and (ii) 1,2-aryl migration in 4*H*-pyrans (**3**) yielding the bicyclic product (**4**) by a di-π-methane process.[2] We report the novel photochemical behaviour of the 4*H*-pyran derivatives (**5**).[3]

The 4*H*-pyran (**5a**) was irradiated† for 60 min. The oily residue was flash chromatographed to afford recovered starting material (60 mg, 10%) and three other products. One of these (110 mg, 40%) was readily identified as 3-phenylpropynonitrile[4] and is obviously a fragmentation product. This was substantiated by the isolation of the other fragment (150 mg, 46%) that was identified as the enamide (**6**).[5] The structure of the third compound (160 mg, 27%) was less easy to assign although mass spectroscopy showed it to be isomeric with the starting material. The i.r. spectrum of this compound showed the presence of an amide (1660 cm^{-1}), eliminating the possibility that it is a 2*H*-pyran, *e.g.* (**7**). The ^{13}C n.m.r. spectrum, which showed four high-field saturated carbon atoms (δ 23.5, 23.7, 31.0, and 34.7) for the cyclopentane ring, two deshielded saturated carbon atoms (δ 55.0 and 60.7), two alkene carbons (δ 113.0 and 150.8) as well as signals for two cyano groups, one amide, and one phenyl ring, is only



(1)



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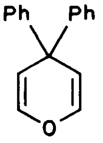

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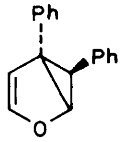

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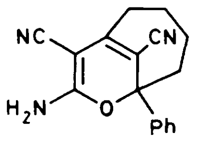
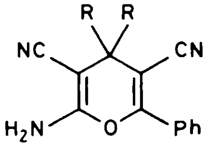
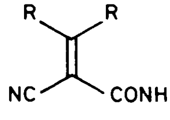


(7)

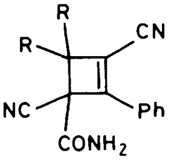


(5)

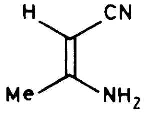


(6)

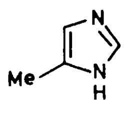
a; RR = $[CH_2]_3$
b; RR = $[CH_2]_4$
c; R = Me



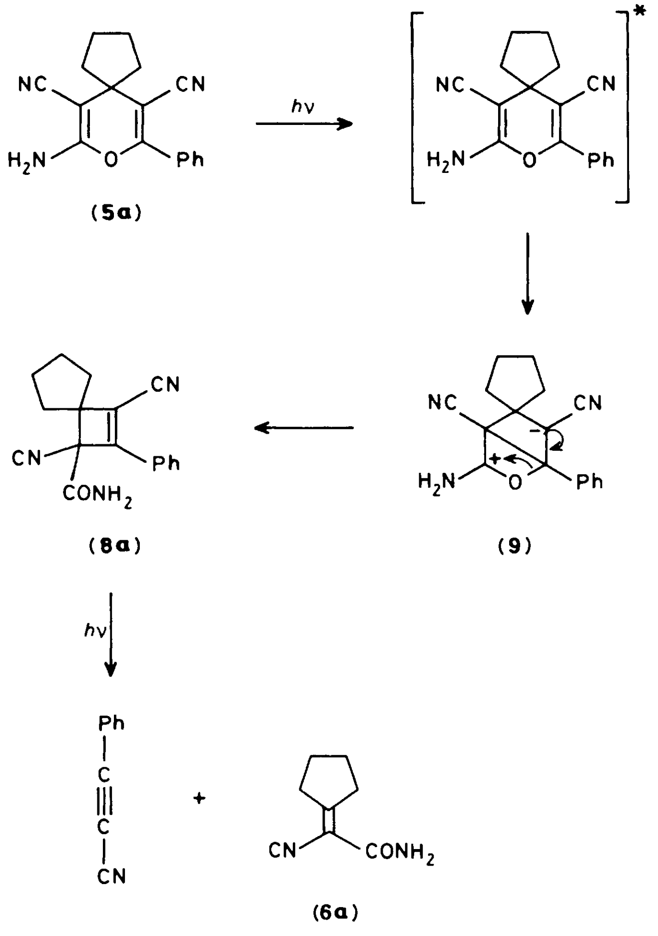
(8)



(10)



(11)



Scheme 1

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† Irradiations (*ca.* 1 h) of the 4*H*-pyrans (600 mg) in methylene chloride (380 ml) were carried out in a conventional immersion well apparatus with a Pyrex filter and a 400 W medium pressure Hg arc lamp. The solutions were deaerated with nitrogen prior to and during irradiation.

compatible with the spirocyclobutene (**8a**).[‡] The formation of the three products could be the result of divergent photochemistry of the 4*H*-pyran (**5a**). However, this possibility can be excluded because independent irradiation of (**8a**) affords the two fragmentation products 3-phenylpropynonitrile and the enamide (**6a**).

The ring contraction of a 4*H*-pyran to a cyclobutene is, as far as we are aware, quite novel. Of all the routes considered for the formation of the cyclobutene, such as C–O bond fission or a di-π-methane–carbene route, the one favoured is shown in Scheme 1. This path exclusively forms the cyclobutene by a process which could involve an electron transfer. Bonding in the radical cation–radical anion affords the more stabilized zwitterion (**9**), which collapses to the cyclobutene (**8**). Secondary photolysis of the cyclobutene follows the fission path exclusively to yield the alkyne and the enamide. Such a fission path has previously been observed for bicyclo[3.2.0]-hept-6-ene and bicyclo[4.2.0]oct-7-ene.[6]

Similar behaviour is seen for the 4*H*-pyran (**5b**) which yields cyclobutene (**8b**)[‡] and the fission products, enamide (**6b**) and 3-phenylpropynonitrile. The reaction described here is not restricted to the spiro-4*H*-pyrans but also occurs for the 4,4-dimethyl derivative (**5c**) again yielding a cyclobutene (**8c**),[‡] 3-phenylpropynonitrile, and the enamide (**6c**).

The ring contraction behaviour of the 4*H*-pyrans is new and probably a result of the particular substitution on the pyran derivatives. It is also noteworthy that the observed reactivity is in clear contrast with the photochemistry of related systems such as the enaminonitriles (**10**) which undergo cyclization to imidazoles (**11**).[7]

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[‡] All the cyclobutenes (**8**) give satisfactory microanalytical data. *Spectroscopic data* for (**8a**): m.p. 148—149 °C (from ethanol); i.r. ν_{max} (KBr) 3380—3180 (NH_2), 2240 (CN), 2200 (CN), 1660 ($CONH_2$), 1610 cm^{-1} ($CONH_2$); ^1H n.m.r. (CD_3SOCD_3) δ 1.7—2.1 (8H, m, CH_2), 7.5 (5H, s, ArH), 7.8 (2H, br.s, NH_2); ^{13}C n.m.r. (CD_3SOCD_3) δ 23.5, 23.7, 31.0, 34.7, 55.0, 60.7, 113.0, 116.2, 116.7, 126.4, 128.6, 129.5, 132.1, 150.8, 164.9; *m/z* 277 (76%) M^+, 276 (100), 260 (12), 259 (15), 249 (41), 248 (47), 233 (44); (**8b**) m.p. 155—156 °C (from ethanol); i.r. ν_{max} (KBr) 3400—3200 (NH_2), 2240 (CN), 2200 (CN), 1660 ($CONH_2$), 1620 cm^{-1} ($CONH_2$); ^1H n.m.r. (CD_3SOCD_3) δ 1.4—2.1 (10H, m, CH_2), 7.6 (5H, s, ArH), 7.9 (2H, br.s, NH_2); ^{13}C n.m.r. (CD_3SOCD_3) δ 22.5, 23.2, 24.5, 30.2, 34.6, 54.1, 55.1, 114.0, 116.2, 116.5, 126.4, 128.8, 129.4, 132.6, 151.7, 164.3; *m/z* 291 (100%) M^+, 290 (94), 262 (39), 248 (76), 247 (48), 220 (33), 77 (12); (**8c**): m.p. 136—138 °C (from ethanol); i.r. ν_{max} (KBr) 3400—3200 (NH_2), 2240 (CN), 2200 (CN), 1660 ($CONH_2$), 1610 cm^{-1} ($CONH_2$); ^1H n.m.r. (CD_3SOCD_3) δ 1.5 (3H, s, CH_3), 1.7 (3H, s, CH_3), 4.7 (2H, br.s, NH_2), 7.3—7.8 (5H, m, ArH); ^{13}C n.m.r. (CD_3OD) δ 20.8, 24.7, 51.9, 56.1, 113.1, 117.4, 118.8, 127.9, 130.2, 133.1, 151.9, 167.6; *m/z* 251 (52%) M^+, 250 (32), 236 (100), 219 (12), 207 (24), 204 (40), 180 (20) 127 (22).