Photochemistry of Cyclic Azo-compounds: Preparation of Highly Strained Spiro-compounds[1]

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Summary Photofragmentation of spiro-3*H*-pyrazoles (**1**) having ring bridges of different size, affords spiro[2.5]-octatrienes (**2a**—**e**) or spiro[2.6]nonatetraenes (**2f**, **g**), which, in a few cases, undergo an additional [1,7]-H-shift to (**3**) and (**4**).

Spiro-3*H*-pyrazoles can be regarded as cyclic azo-compounds. They eliminate nitrogen after photochemical activation giving rise to a reactive intermediate such as a diradical or carbene species. Irradiation of (**1**) should thus lead to highly strained spiro-compounds. The ring strain introduced by the presence of a cyclopropene unit should be considerable since a comparison of bond angles and lengths (from *X*-ray analysis) in a spiro[2.4]heptatriene with those of cyclopropene itself shows a large distortion in the spiro-compound.† The question of the stability of these strained spiro-compounds, as well as the special bonding arrangements, makes them interesting compounds.

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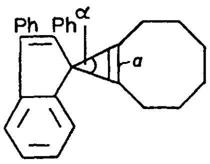
† E. Oeser and H. Dürr, unpublished results: in (A) $\alpha = 49°$, $a = 1{\cdot}27$ Å, compared to $a = 1{\cdot}30$ Å in (B).

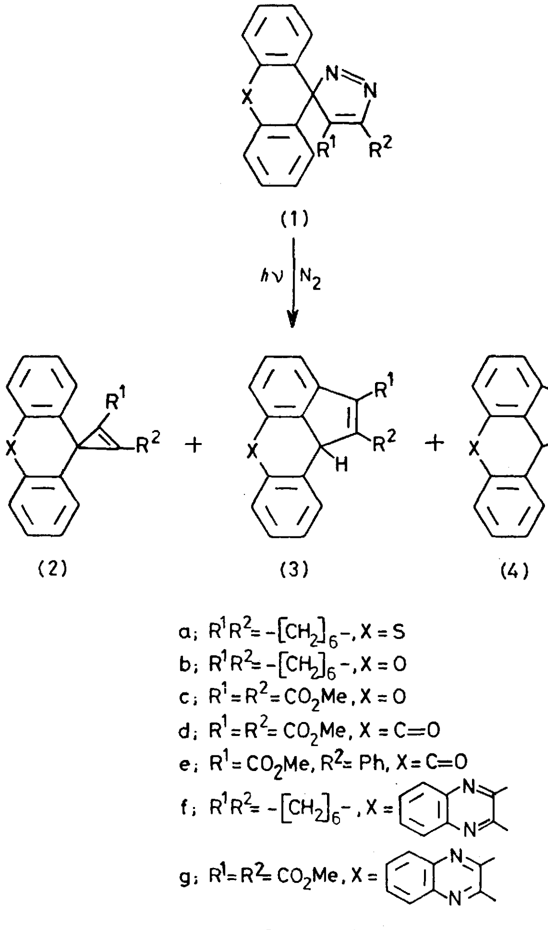


(A)

(B)

Here we report investigations on the photofragmentation of spiro-3*H*-pyrazoles (**1**) bearing an unsaturated 6- or 7-membered ring.

Irradiation (125 W Philips Hg-high pressure lamp) of the spiro-3*H*-pyrazoles[2] (**1a**—**g**) was usually carried out in an ethereal or benzene solution employing Pyrex-filters unless indicated otherwise (see Table) (excitation of the $n\pi^*$-band: 337—360 nm). After evaporation of the solvent the photolysate was chromatographed on silica gel to yield as pure products (after recrystallization) the spiro[2.5]-octatrienes (**2a**—**e**) and spiro[2.6]nonatetraenes (**2f**, **g**) in 8—80% yield.‡ Compounds (**2a**, **b**) are new systems.[3]



Scheme 1

One dibenzo-spiro[2.6]nonatetraene (**2**) (X = CH=CH–) has been prepared previously;[4] however a diester derivative of this strained system was obtained for the first time.

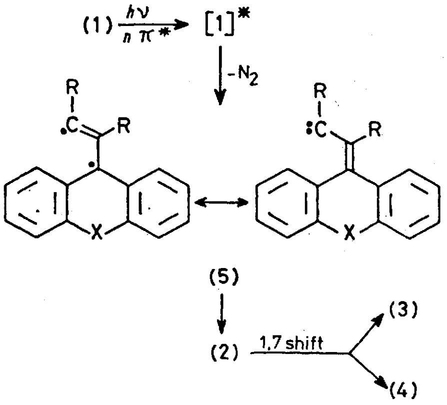
Table

Compound	% Yield (**2**)	(**3**)	(**4**)	ν_{max}/cm^{-1} of (**2**)
a[a,b]	62	—	—	1875
b[a,c,d]	>80	—	—	1865
c[a]	—	7	15	—
d[e]	47	—	—	1840
e[e]	64	—	—	1845
f[e]	13	—	—	1860
g[e,f]	8	9	—	1828

[a] Ethereal solution. [b] Corex-filter. [c] Pyrex filter. [d] Hanovia 500 W lamp. [e] Benzene solution. [f] GW_V filter.

The structure indicated for (**2a**—**e**) follows mainly from the i.r. spectra which exhibit a cyclopropene stretching band at 1828—1875 cm^{-1} (see Table). Further evidence comes from the n.m.r. spectra, which underline the highly symmetrical structure of (**2**).§ However, the novel systems, *e.g.* the spiro[2.6]nonatetraenes (**2f**, **g**), contain a non-planar (boat) seven-membered ring. This is clear from the n.m.r. spectrum of (**2g**) which shows two non-equivalent MeO-groups.¶

In a few cases (*e.g.* **1c**, **1g**) photolysis of (**1**) afforded secondary products the cyclopenta-pyran (**4c**) or the cyclopenta-dibenzo-cycloheptatriene (**3g**).**



Scheme 2

The mechanism for the formation of (**2**), (**3**), and (**4**) is summarized in Scheme 2; either a 1,7-shift or a direct ring closure of (**5**) can be regarded as paths to (**3**) and (**4**).

This paper demonstrates that irradiation of (**1**) is a general route to the spiro-compounds (**2**) (see also ref. 4). Bridges having electron-donating groups (S, O) and electron withdrawing groups (C=O) in (**1**) have no great effect on the yield. A seven-membered ring in (**1**) (see also ref. 3),

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‡ All new compounds gave satisfactory analytical data.

§ (**2a**) n.m.r.: δ 6·9—7·5 (m, 8 Ar H), 2·58 (s, 4H), and 1·80 (s, 8H); mass spectrum: *m/e* 304 (M^+, 54%), 275 ($M^+ - C_2H_5$, 29%), 261 ($M^+ - C_3H_7$, 67%), and 247 ($M^+ - C_4H_9$, 100%).

¶ (**2g**) n.m.r.: δ 2·78 (s, 3H), 4·00 (s, 3H), and 7·48—8·35 (12 Ar H); mass spectrum: *m/e* 434 (M^+, 46%); 403 ($M^+ - OCH_3$, 48%), 375 ($M^+ - CO_2CH_3$, 100%), and 316 ($M^+ - 2CO_2CH_3$, 42%).

** (**4c**) n.m.r.: δ 6·7—7·4 (m, 8H), 3·90 (s, 3H), and 3·27 (s, 3H); this product has also been obtained by G. Ege *et al.*, personal communication.

however, greatly reduces the yield of (**2**). The quinoxalinyl-derivatives (**2f**, **g**) are more stable than simpler systems of (**2**)[4] (X=–CH=CH–). This is probably not related to the photofragmentation but rather to the instability of (**2**).[5]

One can therefore conclude that electronic effects are of no major importance for the stability of (**2**). However ring strain inherent in these systems as a result of the size of the spiro bridge in (**2a**—**e**) as compared to (**2f**, **g**) plays a decisive role.

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[1] For Part 36 of the series Photochemistry of Small Rings see H. Dürr and H.-J. Ahr, *Tetrahedron Letters*, 1977, 1991.

[2] H. Dürr, A. Hackenberger, S. Fröhlich, B. Schley, and H. Weisgerber, unpublished results.

[3] Dihydro-derivative of (**2**): R. H. Maizzoni, Ciba Corp., New York, U.S.P. 3,455,937 (1969).

[4] H. Dürr, A. C. Ranade, and I. Halberstadt, *Tetrahedron Letters* **1974**, **3041**; H. Dürr and H. Schmitz, *Angew. Chem. Internat. Edn.*, 1975, **87**, 674; a diester derivative of (**2**) (X = –CH=CH–) could not be prepared (H. Dürr and B. Weiss, *Angew. Chem.*, 1975, **87**, 674).

[5] J. C. Fleming and H. Shechter, *J. Org. Chem.* 1969, **34**, 3962; E. E. Waali and W. M. Jones, *ibid.*, 1973, **38**, 2573.