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THE AZOXY(AZO)-CHROMOPHORE AS π2-COMPONENT IN PHOTO [2+2] CYCLOADDITION REACTIONS**

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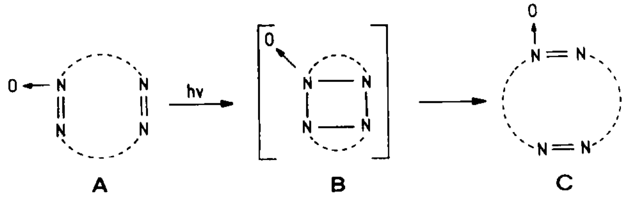
Upon direct (sensitised) excitation selective metathesis is observed for the azoxy/ene 4 (with no intermediate being detectable at -50°C), quantitative [2+2] addition for the azo/ene 2. Thermally 4 undergoes uniform cycloaddition ($t_{1/2}$(18°C) ca. 65 min) to the unusually stable 1,2,3-oxadiazolidine 3 (X-ray).

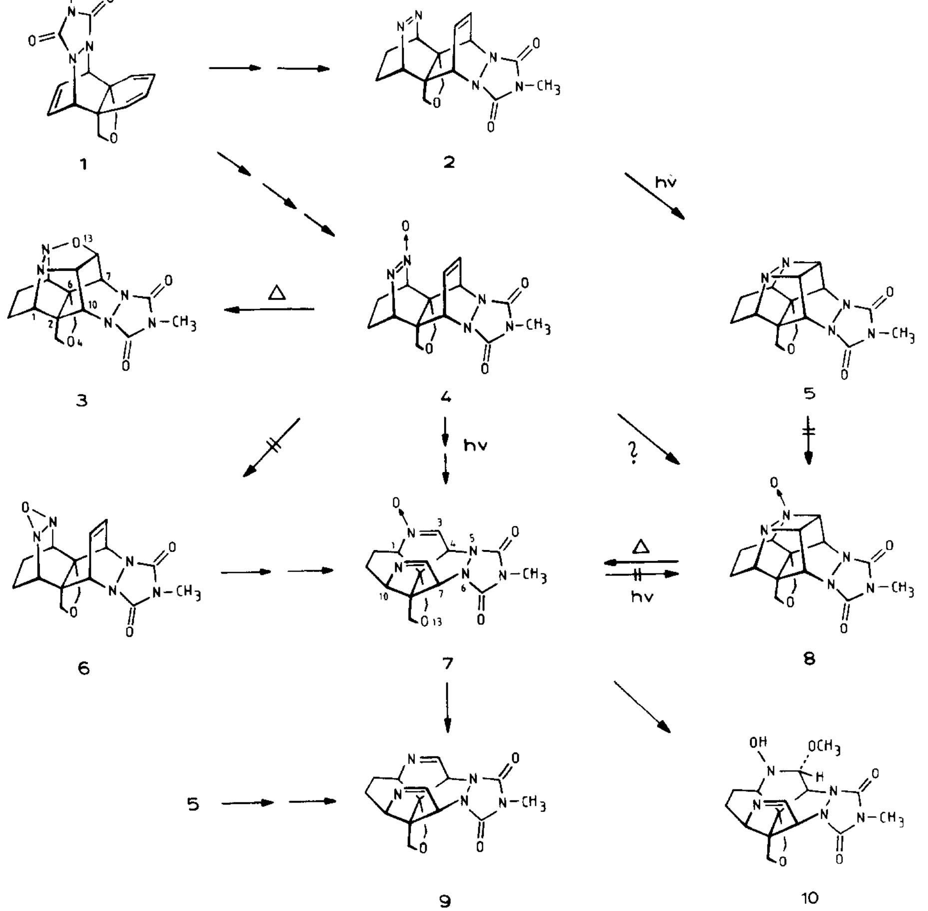
An intramolecular photometathesis involving azoxy/azo-components (A ⟶ C) was recently reported [1], for which no intermediate (e.g. the tetrazetidineoxide B) could be detected between +20 and -70°C [2]. We describe here model experiments with structurally very similar azoxy(azo)/enes (4/2), which should provide more insight into this unprecedented transformation.



The azoxy/ene 4 (λ_{max}(CH_3OH, 0°C)= 225 (6700), 265 nm (sh, 3000, ε_{254}= 3600, ε_{280}= 1400), estimated transannular C-N-distance ca. 2.8 Å [1]) [3] was synthesised starting from 1 (cf. Korat and Ginsburg [4]) by selective diimide reduction (80-85%), oxidative saponification (80%) and addition of 4-methyl-1,2,4-triazolinedione (-10°C; exclusively anti [5], 100%); this route is preferable to the (unspecific) oxidation of azo/ene-2, which is obtained from 1 in 85% yield [4]. 4 is thermally very labile: With $t_{1/2}$ = ca. 65 min at 18°C it undergoes [3+2] addition to the 1,2,3-oxadiazolidine 3 (100%, m.p. > 350°C [6], crystal structure analysis: Fig. 1 [7]), which remains unchanged up to 220°C (pyridine/benzene 1:1). No similar behaviour was observed in the case of azoxy/azo-A when heated up to 160°C.

When 4 is irradiated under the conditions used for the conversion A ⟶ C (10^{-3}M degassed methanolic solutions, -50°C, monochromatic (λ= 254 nm, low pressure Hg lamp, Hanau TNN 15/32, quartz) or polychromatic light ($\lambda \geq$ 280 nm, high pressure Hg lamp, Hanau TQ 150, solidex) up to ca. 60% conversion (besides at best traces of 10 and of polymers) only the metathesis-isomer 7 (colourless crystals, m.p. 170°C, λ_{max}(CH_3OH)= 233 nm (ε= 10500); ε_{254}= 3400; ε_{280}=

200) is observed (DC, ^{1}H nmr; 85-94% isolated based on conversion); at higher conversions (e.g. 90%) increasing amounts of the CH_3OH-adduct 10 (45%, colourless crystals. m.p. 226°C) are formed in addition to traces of polymeric material arising from the thermally unstable pyrrolines 8). In analogous experiments in aprotic CH_3CN-solutions (10^{-3}M) up to ca. 50% conversion again only (DC, ^{1}H nmr) 7 is found. Careful ^{1}H nmr monitoring at -50°C



(250 MHz) in ca. 10^{-2}M CD_3OD (20% $CDCl_3$)-solutions did not reveal any intermediate oxadiaziridine 6 9) or diazetidineoxide 8 (3 as well as 5 remain unchanged under the irradiation

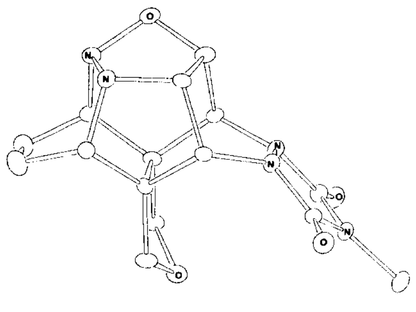
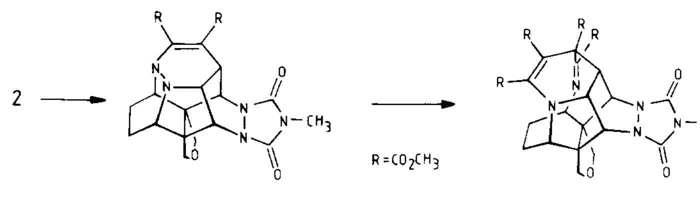


Fig. 1 Molecular structure of the oxadiazolidine 3. The two molecules in the asymmetric unit differ mainly in the bond lengths C2-C6 (1.592, 1.562 Å) and C6-C7 (1.482, 1.572 Å) (C11-C12: 1.552(1.565); C12-O13:1.415(1.417); O13-N14:1.389 (1.377); N14-N15:1.488(1.464);N15-C11:1.490 (1.502) Å). O13 lies 0.58 (0.64) Å above the C11 C12N14N15-plane.

conditions). After irradiation of a 10^{-3} M acetone solution (TQ 150, solidex, $\lambda \geq$ 280 nm, -50°C) 7 is the exclusive, very quickly formed product (83% isolated based on 70% conversion). 7 is photoinert under these conditions; as judged e.g. by the $J_{3,4}$(2.8 Hz) and $J_{7,8}$ (2.3 Hz) values the six-membered rings in 7 are quasi-planar forcing the C=N double bonds ca. 4 Å apart. It seems probable, that 8, if intermediate, is thermally, not photochemically transformed into 7. To test this hypothesis the independent synthesis of (transient) 8 via the 1,2-diazetidine 5 was attempted. The latter is formed quantitatively (colourless crystals, m.p.>350°C) from 2 (λ_{max}(CH_3OH)= 388 (125), 269 (3800, ε_{280}= 1900, ε_{254}= 1700)) by azo/ene-photocycloaddition 10) under the conditions employed for 4 (and which had caused fast N_2-elimination in the bis-azo-analogue 18). 5 cycloreverses above 100°C ($t_{1/2}$ (140°C) ca. 20 min) to the bis-pyrroline 9, which quickly polymerises and is characterised only in solution (^1H nmr); it, however, resists oxidation even in the presence of very powerful reagents (e.g. CF_3CO_3H/Na_2HPO_4, 20°C, 3d; 35 perc. H_2O_2, 20°C,3d; m-chloroperbenzoic acid/$CHCl_3$, 20°C,7d). With the formation of 8 being energetically clearly disfavored its high kinetic lability (relative to 5 increase of torsional/angle strain, of electrostatic interaction, better stabilisation of the aminyl/nitroxide diradical intermediate) 11) becomes less conspicuous. With respect to the original preparative goal - isolation (direct observation) of a tetrazetidine-ring by photo-azo/azo-cycloaddition - this would mean that the oxidation of one azo-component (e.g. A) which is the prerequisite for the photocycloaddition massively destabilises the photoproduct (B).

The favorable structural situation in 2(4) for transannular bond formation 12) is also manifested by thermal additions of the formal[2+2+2] type. 2 reacts quickly with dienophiles, e.g. dimethyl acetylenedicarboxylate (DMAD) 13): With 1 equiv. DMAD (20°C) a ca. 1:3 mixture (80%) of 11 (yellow crystals, m.p. 218°C,λ_{max}(CH_3CN)= 350 nm (ε= 1200)) and 12 (colourless crystals, m.p. 275°C,λ_{max}(CH_3CN)= 360 nm (ε= 3800)), with 5 equiv. DMAD exclusively the latter (85%) is isolated. With 4-methyl-1,2,4-triazolinedione (0°C) the corresponding [2+2+2] adduct is not observed (formed); exclusive product (75%) is the bis-urazole 13 14).



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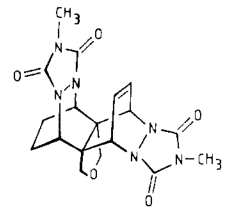

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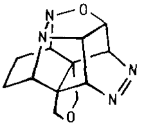
** Photochemical Transformations, Part 62.- Part 61 1).

1) H. Prinzbach, G. Fischer, G. Rihs, G. Sedelmeier, E. Heilbronner, Yang Z.-z., Tetrahedron Lett. (1982) 1251; cit.lit.; cf. J.M. Mellor, R.N. Pathirana, J.H.A. Stibbard, ibid. (1982) 4489; J. Chem. Soc. Perkin I (1983) 2541, 2545.

2) The azo/azo-substrate 18 proved stable under irradiation at -180°C (MTHF, monochromatic light of 254, 365, 405 nm; polychromatic light of $\lambda \geq 280$ nm, Prof. Dr. G. Kaupp). Azoxy/azo /enes (A,4) are being studied.

3) The new compounds are fully analysed (elemental analysis, IR, UV, MS, ^{1}H-, ^{13}C-NMR). 3/5 are additionally characterised as azo-derivatives 14/15 and DMAD adduct 16.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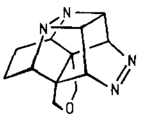
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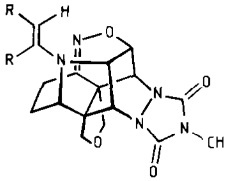
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4) M. Korat, D. Ginsburg, Tetrahedron 29 (1973) 2373; D. Ginsburg, Propellanes, Verlag Chemie, Weinheim, 1975.

5) Experiments are undertaken to enforce syn-additions through massive steric hindrance on the anti-face; G. Fischer, Dissertation, Univ. Freiburg, in preparation.

6) This is remarkable since aliphatic 1,3-azoxy-dipols could not be added to alkenes. The 1,2,3-oxadiazolidines which are formed from "aromatic" azoxy-compounds and alkines (S.R.Challand, C.W. Rees, R.C. Storr, J. Chem. Soc., Chem. Commun. (1973) 837) or alkenes (R. Huisgen, F. Palacios Gambra, Chem. Ber. 115 (1982) 2242, cit. lit.) are highly unstable and only indirectly characterised.

7) Crystals are triclinic, space group P$\bar{1}$ (Nr. 2), a= 7.586, b= 13.652, c= 16.761 Å; α= 106.74, β= 93.14, γ= 103.73°; Z=4; 4794 independent reflections, R=0.132. The asymmetric unit contains two molecules. Because of the instability of the crystals the H-atoms were not localised.

8) E.g. H. Poisel, Monatsh. Chem. 109 (1978) 925.

9) H. Olsen, C.L. Pedersen, Acta Chem. Scand. B 36 (1982) 701: A half-life of 30 min at -24°C was determined for the oxadiaziridine produced by photolysis of the 2,3-diazabicyclo[2.2.2]oct-2-ene-N-oxide; cf. W.R. Dolbier,Jr., K. Matsui, H.J. Dewey, D.V. Horak, J. Michl, J. Am. Chem. Soc. 101 (1979) 2136.

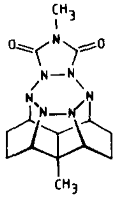
10) Prof. D. Ginsburg has kindly informed us (Oct., 1983), that his collaborator Dr. J. Kettenring has observed [2+2] addition in an analogous substrate: Cf. B. Albert, W. Bernińg, Ch. Burschka, S. Hünig, H.-D. Martin, F. Prokschy, Chem. Ber. 114 (1981) 423,cit. lit.; L.A. Paquette, R. Carr, P. Charumiland, J.F. Blount, J. Org. Chem. 45 (1980) 4922.

11) R. Richter, H. Ulrich, "Four-Membered Rings Containing Two Nitrogen Heteroatoms" in 'The Chemistry of Heterocyclic Compounds', Small Ring Heterocycles, Part 2, Wiley, N.Y.1983, p. 443; E. Schaumann, R. Ketcham, Angew. Chem. Int. Ed. Engl. 21 (1982) 225.

12) Analogous [3+2]- and [2+2] additions were performed with substrates, in which the tetrahydrofuran ring of 2/4 is replaced by a cyclobutane ring.

13) R.M. Acheson, N.F. Elmore, Adv. Heterocycl. Chem. 23 (1978) 263; cit. lit.

14) The azo/azo-molecule 18 reacts with methyltriazolinedione (cp. 13) to give the mono-(20°C)/bis-urazole (100°C) 1)(it was hoped that access to 17 would be favored in a way similar to 11); with DMAD(20°C) the regioselectively formed (via the highly nucleophilic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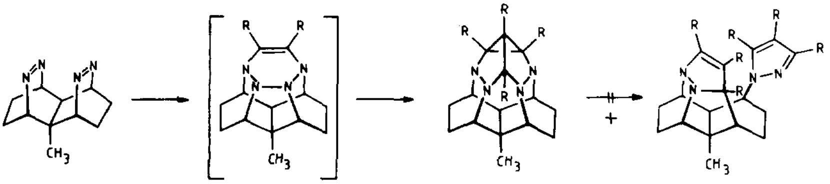
18 19 R=CO_2CH_3 20 21

1:1-adduct 19?) 1:2/1:3-adducts 20/21 (15/50%) are isolated. It is mechanistically informative that a 1,6-diene of type 27/18 does not add DMAD.

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