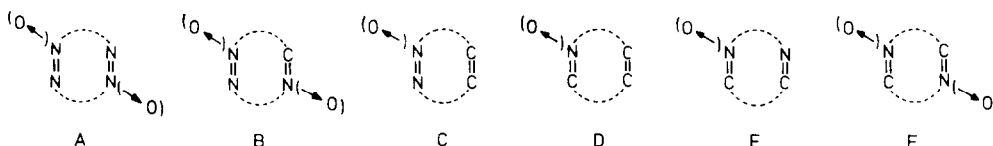


AN INTRAMOLECULAR IMINE/ENE - PHOTO-[2+2]-CYCLOADDITION REACTION**

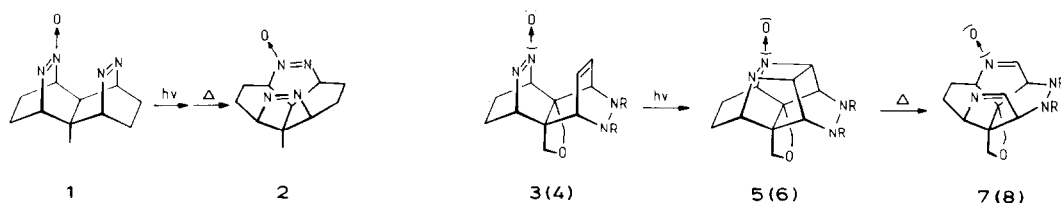
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SUMMARY: In a conformationally rigid cage substrate (15), a clean imine/ene photo-[2+2]-cycloaddition was effected by direct or sensitized (acetone) excitation.

In our search for (preparatively useful) photo-[2+2]-cycloaddition reactions with the more unusual chromophoric systems A-F (as well as benzo-annelated structures ¹⁾), photometathesis had been observed with the azoxy/azo-



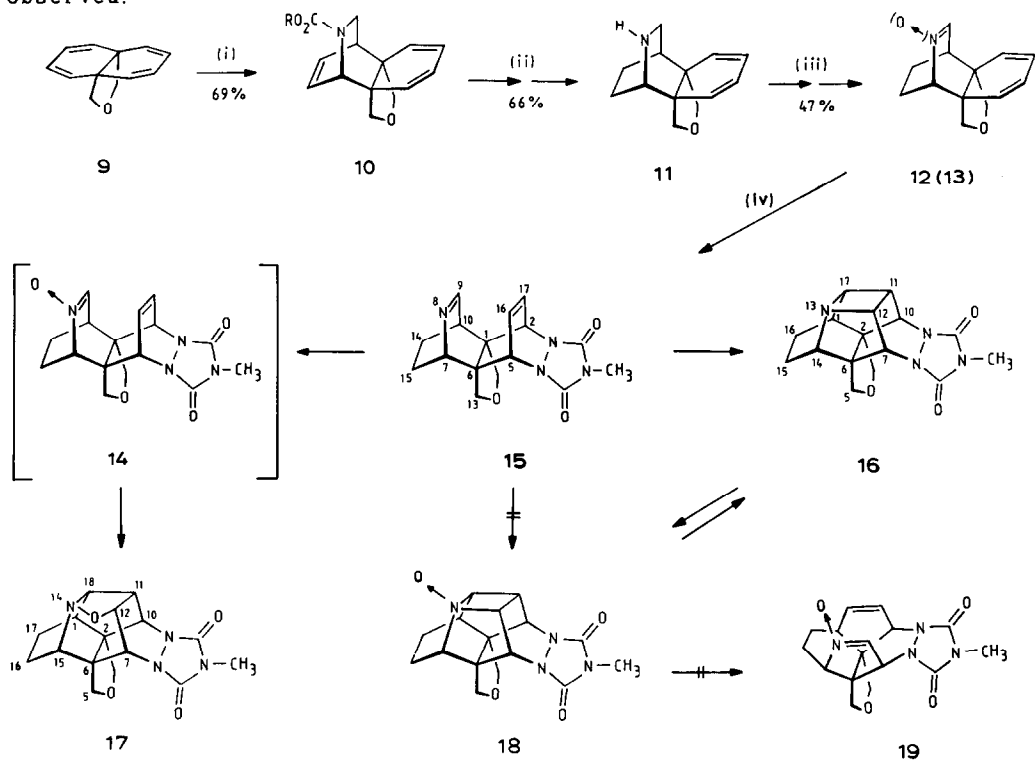
and azoxy/ene-compounds ²⁾ and ⁴ ³⁾. The destabilization of the tetrazetidine-N-oxide ⁴⁾/diazetidene-N-oxide-intermediates by their N-O-functionality was demonstrated with the thermally rather stable diazetidine 5 (t_{1/2}(140°C) ca. 20 min). This compound resisted peracid oxidation to 6 and upon treatment with ozone at -80°C yielded quantitatively the metathesis product 8. Neither 7 nor 8 (E) underwent C=N/C=N(O)-cycloaddition upon direct (λ = 254 nm, CH₃CN, 0°C) or sensitized (acetone) excitation ⁵⁾. Indeed, no intramolecular [2+2]-cyclo-



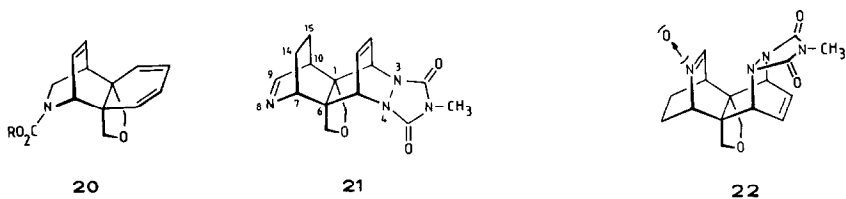
addition with an imine-π₂-component appears to be known and with intermolecular photocycloadditions to imines ⁶⁾ conjugation of the C=N-bond with an electron withdrawing group seems to be essential. In this communication, we report the efficient intramolecular photo-[2+2]-cycloaddition in an (alkyl)imine/ene-system of type D (15).

The synthesis of the syn-imine(nitron)/ene-structures 15 (14) ⁷⁾ was designed after the one described for 3 (4) ²⁾. Its preparative value profits from the fact that of the three cycloaddition steps, one (9→10) ⁸⁾ is highly face-selective (7% syn-adduct 20) and two (12 (13)→15(14)) are face-specific ⁹⁾. From a practical viewpoint it was advantageous to separate and characterize 20

at the stage of the *N*-methyltriazolinedione (NMTD)-adducts 15/21 (21 : m. p. 260°C, $\lambda_{max}(\text{CH}_3\text{CN}) = 248 \text{ nm}$ ($\epsilon = 4600$); typical NMR-differences are $\delta = 3.56$ (br. s, 7-H), 3.97 (br. s, 10-H, $J_{9,10} \leq 0.5 \text{ Hz}$). The isomers 22 were of interest as intermediates to azo (azoxy)/imine-systems of type B¹⁰). The imines 12 (m. p. 107°C)/15 (m. p. 89°C) are thermally rather stable crystalline compounds. The nitron 14 undergoes the intramolecular 1,3-dipolar cycloaddition (to give the isoxazolidine 17) far more readily than the azoxy/ene 4 and therefore could not be studied photochemically: upon NMTD addition to the nitron 13 (obtained from diene 11 and $\text{Na}_2\text{WO}_4/\text{H}_2\text{O}_2$ ¹¹) at -70°C, only 17 (m. p. 240°C) was observed.



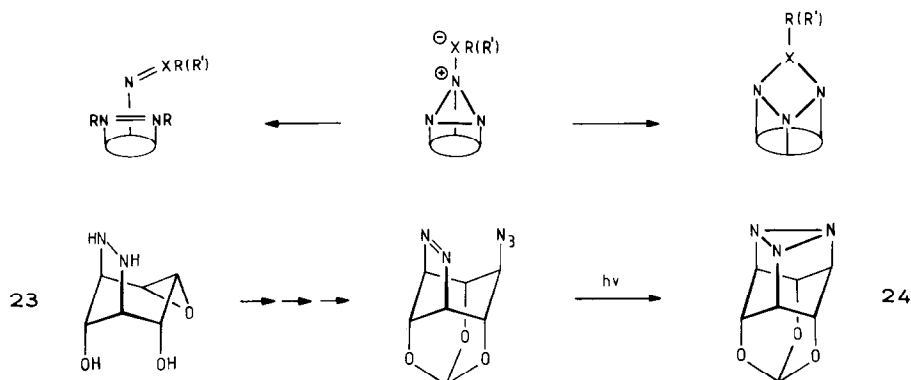
(i): $\text{H}_2\text{C}=\text{N}-\text{CO}_2\text{Et}/\text{benzene}/\text{BF}_3\text{-etherate}$, refl., 20h; (ii): $\text{HN}=\text{NH}$ (7 equiv., 0°C); $(\text{CH}_3)_3\text{SiI}/\text{CH}_2\text{Cl}_2$, 60°C, 2h, CH_3OH ¹²; (iii): $\text{NCS}/\text{diethylether}$, r. t.; triamino phosphine-imine base¹³/THF, r. t.; (iv): NMTD, r. t.



Imine/ene 15 ($\lambda_{max}(\text{CH}_3\text{CN}) = 256 \text{ nm}$ ($\epsilon = 2970$)) upon direct excitation with monochromatic 254 nm-light (ca. 10^{-2} M degassed CH_3CN -solution, -20°C, Hanau Hg TNN 15 lamp) or sensitized excitation (ca. 10^{-3} M degassed acetone solution, -60°C, Hanau TQ 150 high pressure lamp, solidex filter) was cleanly transformed into the azetidine 16 (80-85% isolated, m. p. 228°C). The latter, in con-

trast to the diazetidine 5, could be oxidized by peracetic acid (0°C, 83%) to the oxide 18, which upon heating up to 160°C did not open to the metathesis isomer 19 (cp. 2,7(8)), but simply lost oxygen to give back 16.

The material presented in this paper is part of a program directed towards the synthesis of the still unknown tetra(tri)azetidene ring skeletons by extending the photochemical [2+2]-cycloaddition methodology to N=N(O)/N=N and N=N(O)/C=N-bichromophoric substrates. The limitation to "reluctant" azo-compounds¹⁴⁾ and the kinetic lability inherent in the photoproducts have so far precluded even direct low temperature-identification of the (presumed) intermediates. Besides devising substrates leading to kinetically more stable photoproducts we are currently pursuing ring enlargement of specific (all-cis-alkyl-substituted, rigid) triaziridines¹⁵⁾ by nitrene/carbene-addition as an alternative approach. This could eventually also provide substrates that contain two closely oriented (one "loose end") azo/azo- (A) or azo/imine-units (B)). A representative substrate is the C_{3v}-triaziridine 24 (¹H(¹³C)-NMR (CDCl₃): δ = 5.68 (s, 1H), 5.07 (m, 3H), 4.05 (m, 3H); δ = 101.3 (d, 1C), 78.9 (d, 3C), 53.4 (d, 3C))¹⁶⁾ which was prepared from 23, the adduct of hydrazine to cis-benzenetrifluoride and an intermediate in our streptamine synthesis¹⁷⁾.



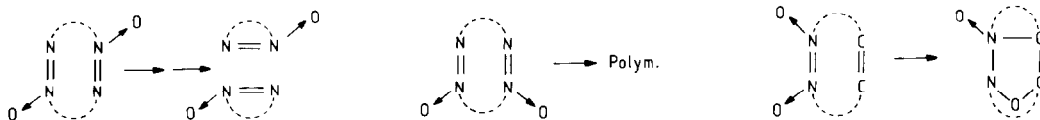
This paper is dedicated to Prof. Dr. R. HUISGEN on the occasion of his 65th birthday as an expression of our good wishes and a mark of our esteem.

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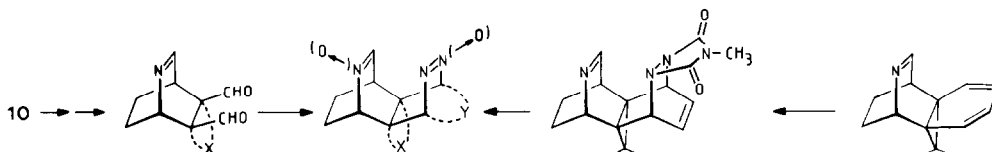
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- 5) In the case of tetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodeca-2,7-diene uniform [2+2]-cycloaddition is observed upon acetone-sensitized excitation: Bulusu A. R. C. Murty, R. Pinkos and H. Prinzbach, in preparation.
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