Formation of 1,3-Diazetidines *via* C–N Dimerization of 4-Cycloalkylidene-oxazol-5(4*H*)-ones in the Solid State

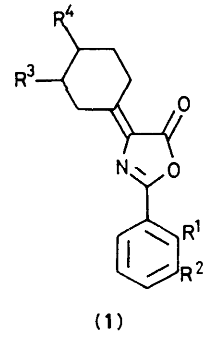
Dirk Lawrenz, Siegfried Mohr,* and Birgit Wendländer

Institut für Organische Chemie der Universität Kiel, Olshausenstrasse 40—60, D-2300 Kiel, Federal Republic of Germany

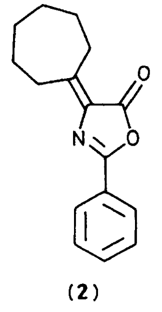
Various 4-cycloalkylidene-oxazol-5(4*H*)-ones have been observed to photodimerize in the solid state *via* an uncommon C–N cycloaddition to give centrosymmetric 1,3-diazetidines in very high yields.

Photodimerization involving C=N double bonds with the formation of 1,3-diazetidines is rarely observed. To our knowledge, there are only two reports in the recent literature, and in both these cases the reactions took place in solution.[1,2] Several early claims, although cited in the recent review literature,[3] were subsequently shown to be incorrect.[4]

4-Alkylidene-oxazol-5(4*H*)-ones exhibit a variety of uncommon radiation-induced reaction types in the solid state, including unsymmetrical dimerizations of glide plane-related monomers with[5a] and without[5b] concomitant H-shift, [2+2]dimerizations to give strained tetraspirocyclobutanes,[5c] solid-state photo-Diels–Alder dimerizations,[5d] and Norrish



(1)



(2)

Table 1. C–N dimerizable 4-cycloalkylidene-oxazol-5(4*H*)-ones.

Compound[a]	R^1	R^2	R^3	R^4	M.p./°C[e]
(**1a**)	H	Me	H	H	102—103
(**1b**)[b]	MeO	H	H	H	101—102
(**1c**)[b]	H	MeO	H	H	99—100
(**1d**)[b,c]	H	H	Me	H	95—96
(**1e**)	H	H	H	Bu^t	116—118
(**2**)[d]	—	—	—	—	86—87

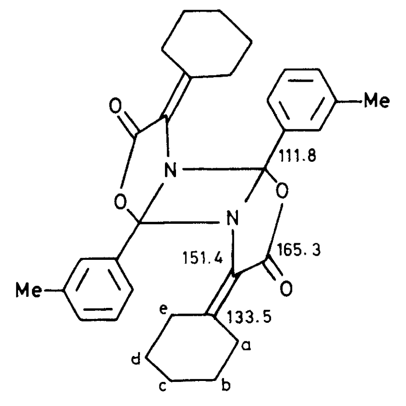
[a] All compounds gave satisfactory C, H, and N microanalyses: i.r. (KBr) $\nu_{C=O}$ 1745—1790 cm^{-1}, two bands (Fermi resonance), the 1780/1790 cm^{-1} band being of higher intensity. [b] A second modification shows a different solid-state reactivity. [c] The corresponding (*E*)-isomer exhibits an unsymmetrical solid-state dimerization of glide plane-related monomers such as described in ref. 5b. [d] O. Tsuge, M. Noguchi, and H. Moriyama, *Heterocycles*, 1982, **19**, 1823; m.p. 88—89 °C. [e] From CH_2Cl_2–MeOH.

type II processes.[5e] We now report that, in addition to these reactions, some 4-cycloalkylidene-oxazol-5(4*H*)-ones such as (**1**) or (**2**) undergo solid-state C–N dimerizations to yield centrosymmetric 1,3-diazetidines of type (**3**) in almost quantitative yields.

The oxazolones in question [(**1a**—**e**) and (**2**) (Table 1)] were prepared by Erlenmeyer condensation of substituted hippuric acids with the corresponding cycloalkanones. The crystals were irradiated with a Philips HPK 125 W lamp (through Pyrex). Though the yields of these solid-state transformations are usually very high (up to 100%), minor residual amounts of the monomers can be extracted with a suitable solvent (acetone; 0 °C), thus leaving the nearly unsoluble pure C–N dimer.

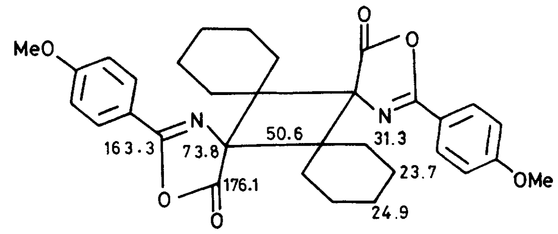
The 1,3-diazetidines (**3**) show a wide range of stability, depending on the substitution pattern. The dimers of (**1b**) and (**1c**), for example, appear to be stable only in the solid state, cycloreverting rapidly to the original oxazolones even in neutral solution. Their t.l.c. (SiO_2; benzene) therefore displays solely the monomer spots. Other dimers are more stable. However, with traces of acids, solutions of all the 1,3-diazetidines (**3**) readily decompose to the monomers. This is in agreement with literature reports, which on the basis of this behaviour regard 1,3-diazetidines as potential systems for solar energy storage.[2]

The proposed centrosymmetrical 1,3-diazetidine structure (**3**) of the dimers is supported by the following arguments. Chemical ionization mass spectra† show the photoproducts to be dimers. On the other hand, ^{13}C n.m.r. spectra display a



(3a)

Figure 1. 1,3-Diazetidine dimer (**3a**) formed from the oxazolone (**1a**): isolated yield 95%; m.p. 221 °C [decomp. to the monomer (**1a**)]; $\nu_{C=O}$ (KBr) 1770 cm^{-1}; δ(^{13}C; 75.5 MHz, $CDCl_3$) 25.6, 27.1, 27.2, 27.3, and 32.4 (C^a—C^e), in addition to those shown.



(4)

Figure 2. Tetraspirocyclobutane-dimer (**4**) originating from a metastable, photoreactive modification of 4-cyclohexylidene-2-(4-methoxyphenyl)oxazol-5(4*H*)-one: isolated yield > 75%; m.p. 220 °C; $\nu_{C=O}$ (KBr) 1800s and 1760w cm^{-1}; δ(^{13}C; $CDCl_3$) values are shown.

single set of atoms, thus indicating the photoproducts to originate from a symmetric C–C (cyclobutane) or alternatively C–N (diazetidine) dimerization.

The ^{13}C n.m.r. spectra allow one to differentiate between a cyclobutane [*e.g.* (**4**)] and a 1,2- or 1,3-diazetidine structure [*e.g.* (**3**)]. A comparison of the chemical shifts (Figure 1 and 2) rules out a cyclobutane structure analogous to (**4**), whose structure has already been determined by *X*-ray analysis.[5c]

In principle, solid-state C–N dimerization can lead to four different products, either 1,2- or 1,3-diazetidines with symmetry types *m*, 2, or $\bar{1}$. A solid-state pairing *via* a two-fold axis is very rarely observed, however, since it does not allow formation of a close-packed structure of irregularly shaped molecules.[6] Hence a quantitative topochemical dimerization as in the former cases to diazetidines with two-fold symmetry appears to be extremely unlikely. Thus the symmetry types *m* or $\bar{1}$ only for the observed photodimers have to be considered.

A mirror symmetry is impossible owing to the observed quantitative yield of these solid-state dimerizations. A random dimerization in a stack of translational oriented monomers finally leads to the presence of isolated monomers, the statistical content of these monomers being 13.5% ('Flory limit').[7] In contrast, the t-butyl-cyclohexylidene-oxazolone (**1e**), for instance, shows no detectable amounts of the original monomer after 4 h of irradiation, even by t.l.c. During this quantitative solid-state conversion, the morphology of the permanently transparent crystals remains intact, so the reaction might be a single crystal-to-single crystal trans-

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† Measured with a Finnigan MAT 8230 spectrometer with isobutane or NH_3 as reactant gas by Dr. U. Rapp, Finnigan MAT, D-2800 Bremen, F.R.G. Conventional electron-impact mass spectra do not show fragments above *M*/2 even at low eV.

formation. These arguments suggest that the solid-state dimers of the oxazolones (**1a**—**e**) are the 1,3-diazetidines (**3**) with inversion symmetry.

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