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THE REACTIONS OF CARBONYL YLIDES WITH AZODICARBOXYLIC ESTERS

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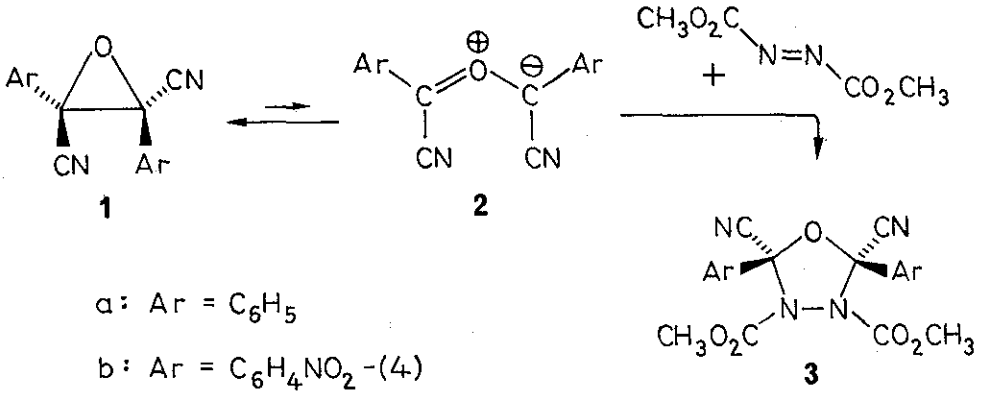
Dedicated to Ken'ichi Takeda on the Occasion of His Seventieth Birthday

The carbonyl ylides, generated by thermal electrocyclic ring opening of 2,3-diaryl-2,3-dicyanooxiranes, combine with azodicarboxylic esters to give primary cycloadducts which eliminate aroyl cyanide and produce α-cyanoarylidenehydrazine-$\underline{N}^{\beta},\underline{N}^{\beta}$-dicarboxylic esters. Whereas the dimethyl esters are thermostable, the diethyl esters undergo a fragmentation to ethyl α-cyanoarylidenehydrazine-$\underline{N}^{\beta}$-carboxylate besides ethylene and carbon dioxide.

Azomethine ylides, which occur in a thermal equilibrium with suitably substituted aziridines, undergo 1,3-dipolar cycloadditions to azodicarboxylic esters to yield stable 1,2,4-triazolidine derivatives.[1] Analogously, the substituted oxiranes $\underline{1}$ entertain thermal equilibria with small concentrations of the car-



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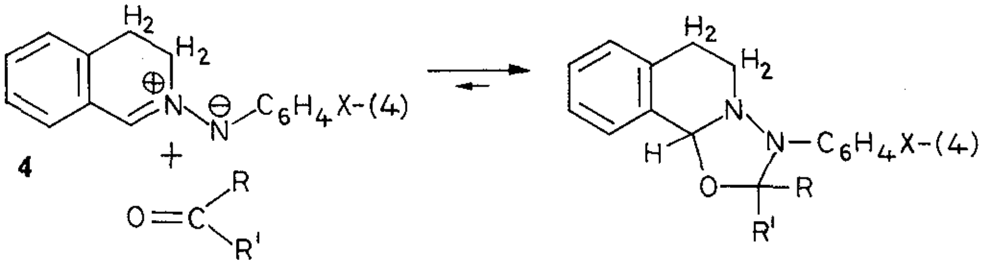
a: Ar = C_6H_5

b: Ar = $C_6H_4NO_2$-(4)

bonyl ylides 2.[2] The reactions of 1a and b with dimethyl azodicarboxylate at 120-130°C provided compounds $C_{12}H_{11}N_3O_4$ (54 %, mp 114.5-116°C) and $C_{12}H_{10}N_4O_6$ (50 %, mp 118.5-120°C), respectively. The expected cycloadducts, the 1,3,4-oxdiazolidines 3, probably suffered elimination of aroyl cyanide. It has been demonstrated that the cycloaddition of the azomethine imines 4 [3] to carbonyl compounds is reversible.[4] Thus, the 1,3-dipolar cycloreversion of 3 should yield the azomethine imines 5 or their stabilization products.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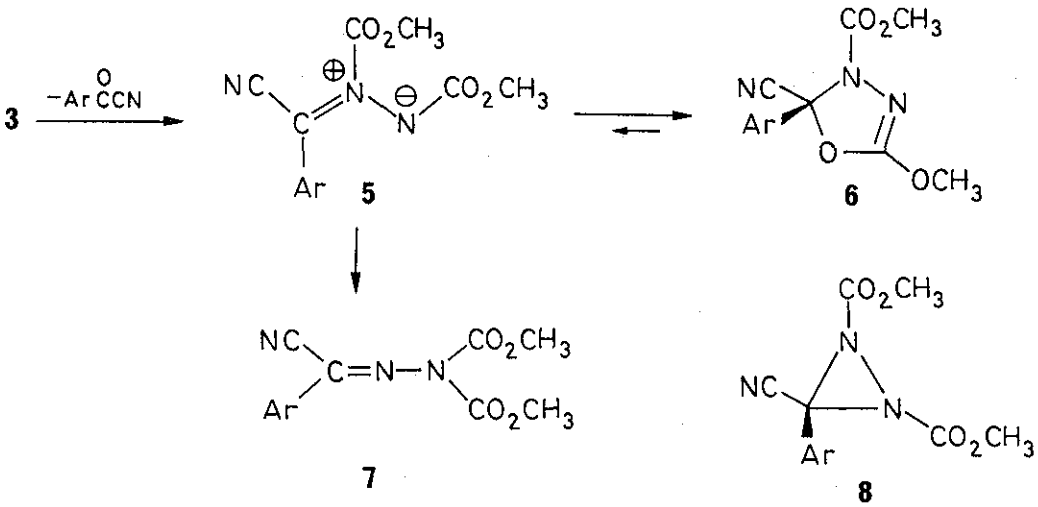
Azomethine imine N^{α},N^{β}-dicarboxylic esters which result from interaction of diazoalkanes with azodicarboxylic esters,[5] can undergo a reversible cyclization to 1,3,4-oxdiazolines of type 6 and an irreversible acyl shift to hydrazone-N^{β},N^{β}-dicarboxylic esters,[6,7] 7 in our example. The properties of the products are indeed in agreement with the hydrazone 7.



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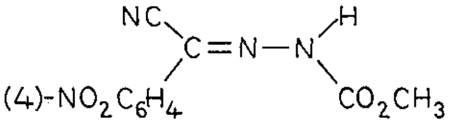
The equivalence of the ester singlets in the nmr spectrum ($CDCl_3$), τ 6.05 for 7a and 6.00 for 7b, is consistent with the hydrazone formulae or the diaziridine structure 8, but not with 5 or 6. The carbonyl frequencies (KBr) are unusually high: 1796 for 7a and 1773 cm^{-1} for 7b; the bond system of 7 corresponds to a diacylimide. The uv spectra (ethanol) allow us to discard 8 in favor of 7: λ_{max} (log ε) = 275 (3.91) for 7a, 323 (3.91) and 275 nm (4.07) for 7b. The uv maxima depend only slightly on solvent polarity.

The reaction of α-diazophenylacetonitrile with dimethyl azodicarboxylate at 70°C produced a specimen identical with 7a: the low yield (2 %) limits conclusions. Stronger chemical evidence for 7b comes from the 92 % conversion to the monoester 9 (mp 194-199°C dec.) in refluxing methanol (48 hr). The ir spectrum of 9 (KBr) shows bands at 3125 for NH, 2215 for C≡N and 1724 cm^{-1} for C=O; the acidic NH appears in the nmr at τ -0.5. The uv band of 9 at 321 nm (log ε 4.35) undergoes a bathochromic shift by 89 nm on deprotonation to the orange anion (410 nm, log ε 4.35) with $NaOC_2H_5/C_2H_5OH$.



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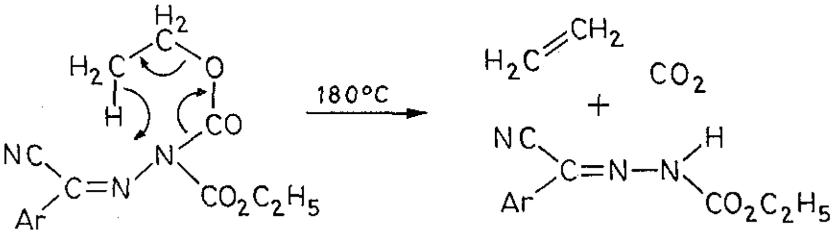

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a : Ar = C_6H_5 b : Ar = $C_6H_4NO_2$-(4)

Whereas the dimethyl ester 7a is stable at 180°C, the corresponding diethyl ester 10a, produced from 1a and diethyl azodicarboxylate at 180°C, undergoes elimination of CO_2 and ethylene affording 11a (mp 94-96°C) in 51 % yield. Fragmentations in the pyrolysis of *ethyl* esters were formulated via cyclic electron shifts as early as 1938.[8] The p-nitrophenyl compound 10b (mp 64-66°C) was accessible from 1b and diethyl azodicarboxylate at 140°C in 60 % yield; at 180°C it was likewise converted to

11b (mp 194-186°C dec.). The 262 peak corresponding to the cation of 11b is the base peak in the mass spectrum of 10b.

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