

THE REACTIONS OF CARBONYL YLIDES WITH
AZODICARBOXYLIC ESTERS

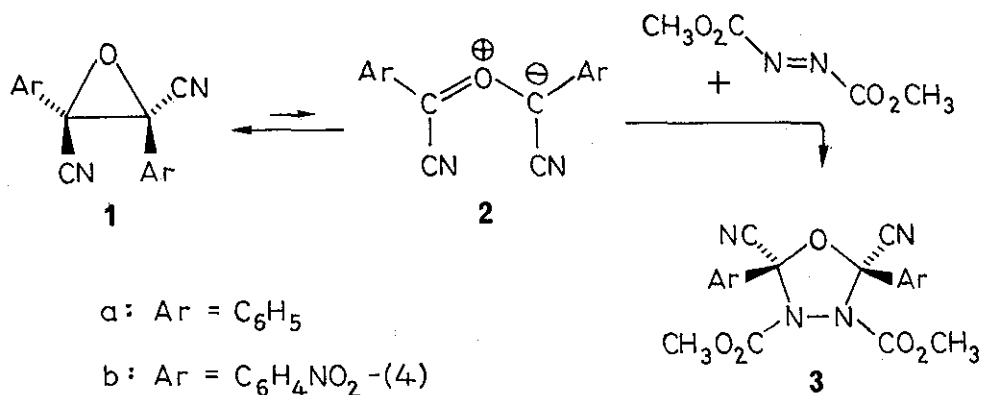
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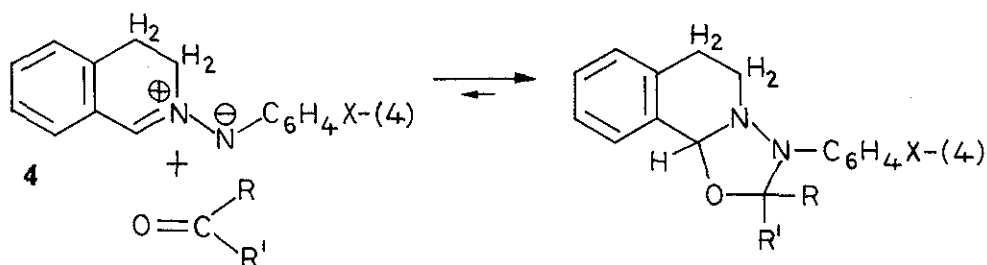
Dedicated to Ken'ichi Takeda on the Occasion of His
Seventieth Birthday

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}^{β} , \underline{N}^{β} -dicarboxylic esters. Whereas the dimethyl esters are thermostable, the diethyl esters undergo a fragmentation to ethyl α -cyanoarylidenehydrazine- \underline{N}^{β} -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 1 entertain thermal equilibria with small concentrations of the car-

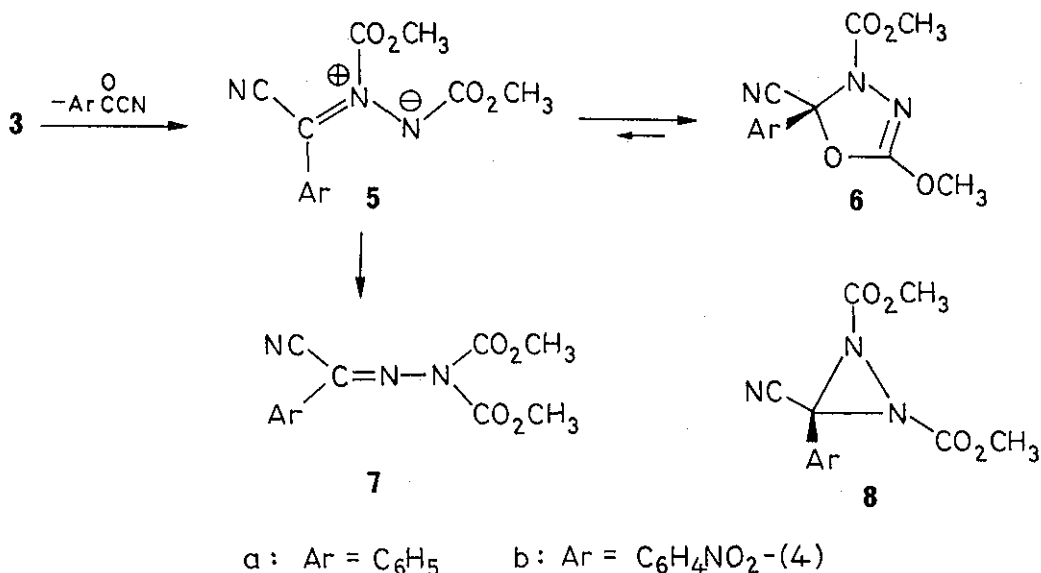


bonyl ylides 2.² The reactions of 1a and 1b with dimethyl azodicarboxylate at 120-130°C provided compounds C₁₂H₁₁N₃O₄ (54 %, mp 114.5-116°C) and C₁₂H₁₀N₄O₆ (50 %, mp 118.5-120°C), respectively. The expected cycloadducts, the 1,3,4-oxdiazolidines 3, probably suffered elimination of aroyl cyanide. It has been demonstrated that the cycloaddition of the azomethine imines 4³ to carbonyl compounds is reversible.⁴ Thus, the 1,3-dipolar cycloreversion of 3 should yield the azomethine imines 5 or their stabilization products.



Azomethine imine $\underline{\text{N}}^{\alpha}, \underline{\text{N}}^{\beta}$ -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- $\underline{\text{N}}^{\beta}, \underline{\text{N}}^{\beta}$ -dicarb-

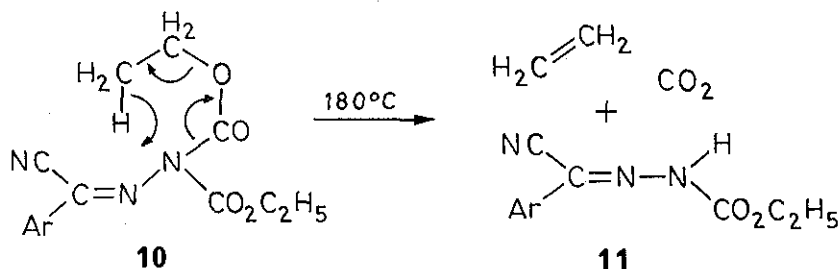
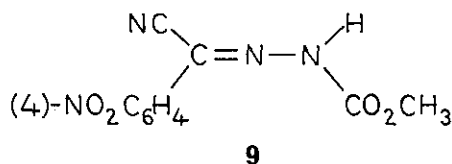
oxylic esters, ^{6,7} 7 in our example. The properties of the products are indeed in agreement with the hydrazone 7.



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} ($\log \epsilon$) = 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 evi-

dence 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 NaOC₂H₅/C₂H₅OH.



a: Ar = C₆H₅

b: Ar = C₆H₄NO₂-(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 CO₂ 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.

REFERENCES

- 1 E. Brunn and R. Huisgen, Tetrahedron Lett., 1971, 473.
- 2 H. Hamberger and R. Huisgen, J.C.S. Chem. Commun., 1971, 1190.
- 3 R. Huisgen, R. Grashey, P. Laur, and H. Leitermann, Angew. Chem., 160, 72, 416.
- 4 R. Grashey and K. Adelsberger, Angew. Chem., 1962, 74, 292.
- 5 E. Müller, Ber. Deut. Chem. Ges., 1914, 47, 3001; H. Staudinger and A. Gaule, ibid., 1916, 49, 1961.
- 6 E. Fahr, K. Königsdorfer, and F. Scheckenbach, Liebigs Ann. Chem., 1965, 690, 138; E. Fahr, K. Döppert, and F. Scheckenbach, ibid., 1966, 696, 136.
- 7 G.F. Bettinetti and P. Grünanger, Tetrahedron Lett., 1965, 2553.
- 8 C.D. Hurd and F.H. Blunck, J. Amer. Chem. Soc., 1938, 60, 2419.

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