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–$N^\beta$, $N^\beta$-dicarboxylic esters. Whereas the di-
methyl esters are thermostable, the diethyl esters under-
go a fragmentation to ethyl α-cyanoarylidenehydrazine–$N^\beta$-
carboxylate besides ethylene and carbon dioxide.

Azomethine ylides, which occur in a thermal equilibrium
with suitably substituted aziridines, undergo 1,3-dipolar cyclo-
additions to azodicarboxylic esters to yield stable 1,2,4-triazol-
olidine derivatives.1 Analogously, the substituted oxiranes 1 en-
tertain thermal equilibria with small concentrations of the car-
The reactions of \( \text{la} \) and \( \text{b} \) with dimethyl azodicarboxylate at 120-130°C provided compounds \( \text{C}_{12}\text{H}_{11}\text{N}_{3}\text{O}_{4} \) (54\%, mp 114.5-116°C) and \( \text{C}_{12}\text{H}_{10}\text{N}_{4}\text{O}_{6} \) (50\%, mp 118.5-120°C), respectively. The expected cycloadducts, the 1,3,4-oxdiazolidines 2, probably suffered elimination of acryl cyanide. It has been demonstrated that the cycloaddition of the azomethine imines \( \text{4} \) to carbonyl compounds is reversible. Thus, the 1,3-dipolar cycloreversion of 2 should yield the azomethine imines 5 or their stabilization products.

Azomethine imine \( \text{N}^{\alpha},\text{N}^{\beta}\)-dicarboxylic esters which result from interaction of diazoalkanes with azodicarboxylic esters, can undergo a reversible cyclization to 1,3,4-oxdiazolines of type 6 and an irreversible acyl shift to hydrazone-\( \text{N}^{\beta},\text{N}^{\beta}\)-dicarb-
oxylic esters,\textsuperscript{6,7} \( Z \) in our example. The properties of the products are indeed in agreement with the hydrazone \( Z \).

The equivalence of the ester singlets in the nmr spectrum (CDCl\(_3\), \( \tau \) 6.05 for \( Z_a \) and 6.00 for \( Z_b \), is consistent with the hydrazone formulae or the diaziridine structure \( S \), but not with \( Z \) or \( S \). The carbonyl frequencies (KBr) are unusually high: 1796 cm\(^{-1}\) for \( Z_a \) and 1773 cm\(^{-1}\) for \( Z_b \); the bond system of \( Z \) corresponds to a diacylimide. The uv spectra (ethanol) allow us to discard \( S \) in favor of \( Z \): \( \lambda_{\text{max}} \) (log \( \varepsilon \)) = 275 (3.91) for \( Z_a \), 323 (3.91) and 275 nm (4.07) for \( Z_b \). The uv maxima depend only slightly on solvent polarity.

The reaction of \( \alpha \)-diazophenylacetonitrile with dimethyl azodicarboxylate at 70°C produced a specimen identical with \( Z_a \): the low yield (2\%) limits conclusions. Stronger chemical evi-
dence for 7b comes from the 92% conversion to the monoester 2 (mp 194-199°C dec.) in refluxing methanol (48 hr). The ir spectrum of 2 (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 δ -0.5. The uv band of 2 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.

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\begin{align*}
\text{NC} & \text{C=N-N} \quad \text{H} \\
\text{(4)-NO₂ C₆H₄ CO₂CH₃} \\
\end{align*}
\]

\[
\begin{align*}
\text{H₂C} & \text{C} \quad \text{O} \quad \text{H₂C} + \text{CO₂} \\
\text{NC} & \text{C=N-N} \quad \text{H} \\
\text{Ar} & \text{CO₂C₂H₅} \\
\end{align*}
\]

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

REFERENCES


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