Octacarbonyldicobalt Induced Conversion of 1,2-Diaroyldiaziridines into Dihydro-oxazoles (Oxazolines)

Dominique Roberto and Howard Alper*

Ottawa-Carleton Chemistry Institute, Department of Chemistry, University of Ottawa, Ottawa, Ontario Canada K1N 9B4

1,2-Diaroyldiaziridines react with octacarbonyldicobalt in benzene, at 65—70 °C, to give dihydro-oxazoles by an intramolecular displacement-rearrangement reaction; thermal rearrangement of the strained-ring heterocycles affords 4,5-dihydro-oxadiazoles.

Organometallic compounds can effect a variety of interesting reactions of heterocyclic substrates.¹⁻³ Three-membered ring nitrogen compounds, for instance, can serve as precursors to larger ring heterocycles by reactions with metal carbonyls, or with carbanions or carbon monoxide in the presence of a metal complex. Examples include the reaction of azirines (1) with octacarbonyldicobalt to give 2-styrylindoles (2)⁴ and with carbanions (of type RCHCO₂R') and hexacarbonyl molybdenum affording succinimides,⁵ and the carbonylation of α -lactams (3) to give azetidine-2,4-diones (4) using octacarbonyldicobalt as a stoicheiometric reagent, or chlorodicarbonylrhodium(1) dimer as a catalyst.⁶



The reaction of saturated three-membered ring compounds, containing two heteroatoms, with metal carbonyls has not been investigated. Diaziridines are one such interesting class of compounds.⁷ It was expected that appropriately substituted diaziridines may undergo ring expansion on treatment with metal carbonyls. We now describe the reaction of 1,2-diaroyldiaziridines with octacarbonyldicobalt to form dihydro-oxazoles in good yields. Diaroyldiaziridines were chosen for this study because they are easy to prepare and handle, and are stable at ambient temperature.

3-Hydromethyl-3-methyldiaziridine (5), readily synthesized by reaction of acetol (1-hydroxypropan-2-one) with hydroxylamine-O-sulphonic acid and methanolic ammonium hydroxide,⁸ reacts with aroyl chlorides (6) in pyridine to give the 1,2-diaroyldiaziridinyl esters (7; R = Me, OMe, or Cl). When (7; R = Me), was treated overnight with an equimolar amount of octacarbonyldicobalt in dry benzene at 65-70°C,† followed by chromatographic work-up, the amidodihydro-oxazole (8; R = Me) was isolated in 51% yield of analytically pure material. Use of a carbon monoxide atmosphere afforded (8) in 79% yield. The analytical and spectral data support the structure assigned to (8; R = Me).[†] It showed NH (3437 cm⁻¹), carbonyl (1662 cm⁻¹), and imine $(1643 \text{ cm}^{-1}) \text{ i.r. stretching vibrations } (C_6H_6 \text{ solution}), \text{ methyl-}$ ene protons as an AB quartet centred at δ 4.58 in its ¹H n.m.r. spectrum, and the methylene carbon ¹³C resonance at δ 78.5. An intense M + 1 peak (at m/z 309) was observed in its chemical ionization mass spectrum.

Dihydro-oxazoles (8; R = OMe) (59%)‡ and (8; R = Cl) (79%)‡ were also isolated from the reaction of (7; R = OMe and Cl) with Co₂(CO)₈, accompanied by the carboxylic acid (9). For instance, *p*-chlorobenzoic acid (9; R = Cl) was obtained in 70% yield with (7; R = Cl) as the substrate. Quantitative thermal rearrangement of the diaziridine to the dihydro-oxadiazole (10)‡ occurred when (7; R = Me, Cl, or OMe) was heated in benzene in the absence of Co₂(CO)₈. The dihydro-oxazole (8) does not arise from (10) since exposure of (10; R = Cl) to Co₂(CO)₈ in benzene at 65–70 °C afforded recovered (10). Use of chloro-dicarbonylrhodium dimer as the

† The following general procedure was used. A mixture of (7) (0.38 mmol) and $\text{Co}_2(\text{CO})_8$ (0.38 mmol) in dry benzene (10 ml) was stirred under nitrogen at 65–70 °C. After 75 min, the reaction was essentially complete (i.r. and t.l.c. monitoring), but stirring was continued overnight. The solution was cooled and filtered, and the filtrate was washed with 1 M NaOH to remove the acid (9) (isolated by acidification of the aqueous layer). The dried benzene layer was concentrated to a small volume by rotary evaporation, and the dihydro-oxazole (8) was purified by preparative t.l.c. (silica gel) using hexane–ethyl acetate (7:3 for R = Me or Cl; 4:6 for R = OMe) as the eluant.

 \ddagger (8), R = Me, m.p. 165–167 °C; R = Cl, m.p. 168–170 °C; (10), R = Me, m.p. 92–94 °C; R = Cl, m.p. 104–105 °C; R = OMe, m.p. 120–122 °C. Satisfactory analytical and spectral data were obtained for (8) and (10). metal carbonyl, in reaction with (7) [10:1 ratio of (7) to Rh] also afforded the thermal product in high yield. In other words, the rhodium complex is inert. The thermal isomerization found here, (7) \rightarrow (10), was previously observed with monoaroyldiaziridines,⁹ the latter heterocycles rearranging at ambient temperature in chloroform, acetonitrile, or methylene chloride. Thermal rearrangement of spirocyclic 1,2-diaroyldiaziridines does not afford dihydro-oxadiazoles, but other products such as β , β -diaroylhydrazones.

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