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

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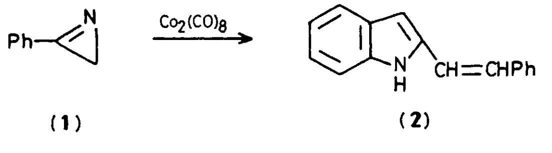
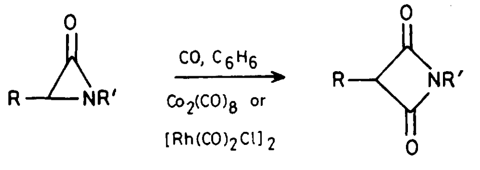
1,2-Diaroyldiaziridines react with octacarbonyldicobalt in benzene, at 65—70 °C, to give dihydro-oxazoles by an intramolecular displacement–rearrangement reaction; thermal rearrangement of the strained-ring heterocycles affords 4,5-dihydro-oxadiazoles.

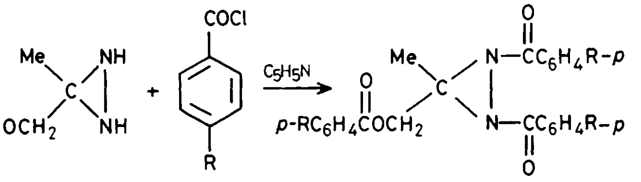
Organometallic compounds can effect a variety of interesting reactions of heterocyclic substrates.[1—3] Three-membered ring nitrogen compounds, for instance, can serve as precursors to larger ring heterocycles by reactions with metal carbonyls, or with carbanions or carbon monoxide in the presence of a metal complex. Examples include the reaction of azirines (**1**) with octacarbonyldicobalt to give 2-styrylindoles (**2**)[4] and with carbanions (of type $R\bar{C}HCO_2R'$) 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(I) dimer as a catalyst.[6]



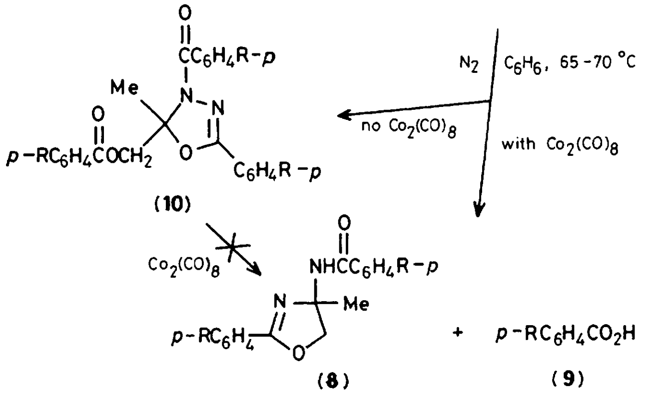
(**1**) (**2**)



(**3**) (**4**)



(**5**) (**6**) (**7**)



(**10**)

(**8**) (**9**)

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 amido-dihydro-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 cm^{-1}) i.r. stretching vibrations (C_6H_6 solution), methylene protons as an AB quartet centred at δ 4.58 in its ^1H n.m.r. spectrum, and the methylene carbon ^{13}C 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 $Co_2(CO)_8$, 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 $Co_2(CO)_8$. The dihydro-oxazole (**8**) does not arise from (**10**) since exposure of (**10**; R = Cl) to $Co_2(CO)_8$ in benzene at 65—70 °C afforded recovered (**10**). Use of chloro-dicarbonylrhodium dimer as the

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† The following general procedure was used. A mixture of (**7**) (0.38 mmol) and $Co_2(CO)_8$ (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.

‡ (**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**) → (**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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