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Unusual Products from Dirhodium Tetraacylate-Catalyzed Decomposition of Diazoacetylcycloalkanes

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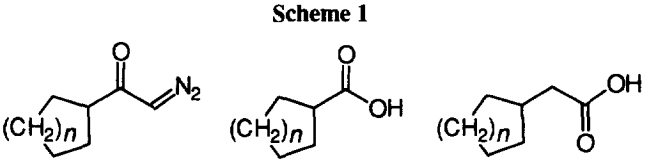
Abstract: $Rh_2(OAc)_4$-assisted decompositions of diazoacetylcycloalkanes are shown to yield cycloalkylacetic acids (Wolff rearrangement), unexpected cycloalkylcarboxylic acids and bicyclic ketones (intramolecular C-H bond insertion). $Rh_2(OCOCF_3)_4$-promoted reactions, on the other hand, have furnished bicyclic ketones and ketene dimers. © 1997 Elsevier Science Ltd.

The interaction of α-diazocarbonyl compounds with dirhodium tetraacetate generates electrophilic carbenoid-rhodium complexes, whose intramolecular insertion into unactivated carbon-hydrogen bonds constitutes a new carbon-carbon bond-forming reaction of interest in organic synthesis.[1,2,3]

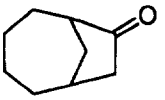
When in connection with a problem of terpene synthesis and need for the preparation of some bicyclic ketones diazoacetylcyclohexane (**1c**)[4] was exposed to decomposition over a catalytic quantity of dirhodium tetraacetate in an inert medium, no C-H insertion product was observed, but acids **2c** and **3c** (ca. 45% of a 2:3 mixture) could be isolated. Similar reactions of diazoketone **1a**[5] as well as of **1b**[6] led to 2:3 **2a/3a** (ca. 50%) and 2:3 **2b/3b** (ca. 42%) mixtures, respectively. Whereas acids **3a**, **3b** and **3c** emanate from hydration of ketenes, the products of Wolff rearrangements of the diazoketones **1**, the formation of acids **2** is unprecedented.[7] It is noteworthy that larger ring compounds gave insertion products [**1d** → **4**[8] (ca. 45%); **1e** → **5b**[9] (ca. 55%); **1f** → **5c**[10] (ca. 40%); **1g**[11] → **5d** (ca. 25%) and **6** (20%)[12] as well as 2:3 acid mixtures [**2d/3d** (ca. 40%); **2e/3e** (ca. 30%); **2f/3f** (ca. 30%); **2g/3g** (ca 25%)].

Scheme 1

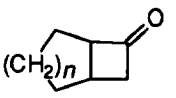


1 **2** **3**

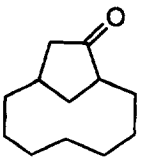
a, $n = 0$; **b**, $n = 1$; **c**, $n = 2$; **d**, $n = 3$; **e**, $n = 4$; **f**, $n = 5$; **g**, $n = 6$



4



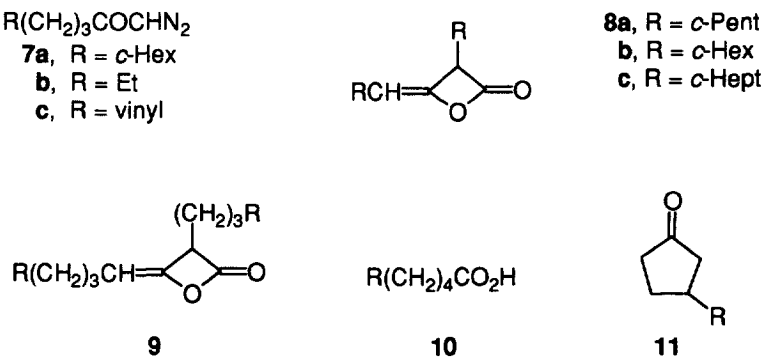
5a $n = 3$
5b $n = 4$
5c $n = 5$
5d $n = 6$



6

In order to gain more insight into the relationship of the catalyst structure and the reaction outcome, diazoketones **1b**, **1c**, **1d** and **7a**, **7b** and **7c**[3] were exposed to decomposition over dirhodium tetratrifluoroacetate. Each of the reactions led to ketene dimers [**8a** (56%), **8b** (68%), **8c** (36%), **9a** (30%), **9b** (16%) and **9c** (18%), respectively] and the ketene hydration products [**3b** (20%), **3c** (12%), **3d** (13%), **10a** (15%), **10b** (17%), and **10c** (35%), respectively]. Furthermore, some of the diazoketones (**1d**, **7a**, **7b** and **7c**) also gave insertion products. Diazo compound **1d** furnished ketones **4** (25%) and **5a** (17%, stereoisomer mixture), while the remaining three diazoketones yielded **11a** (35%),[13] **11b** (33%)[13] and **11c** (44%),[14,15] respectively.

Scheme 2



a, R = *c*-Hex; **b**, R = Et; **c**, R = Vinyl

As the above observations indicate, the formation of cyclic ketones by intramolecular carbon-hydrogen insertion is not the sole mode of decomposition of diazoacetyl compounds under dirhodium tetraacylate catalysis. At least two other decomposition routes exist, one of which is the Wolff rearrangement involving ketene intermediates. In both processes ketene-based products are important, in the case of $Rh_2(OAc)_4$ catalysis appearing as acids (**3**) and under the influence of $Rh_2(OCOCF_3)_4$ manifesting themselves as dimers[16] (**8** and **9**) and acids (**3** and **10**).

The formation of the nor-acids **2** under the influence of Rhodium catalyst is unusual.

It appears that the two catalysts exert a minimal effect on the dissimilarity of the reactions.

EXPERIMENTAL

Melting points were obtained on a micro hot stage and are uncorrected. IR spectra were obtained with $CHCl_3$ solutions. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded at 200.1 and 50.3 MHz, respectively. Column chromatography was executed on 70-230-mesh Merck silica gel. All reactions were carried out under N_2, and all extracts were dried over Na_2SO_4.

Preparation of Diazo Ketones. Freshly distilled oxalyl chloride (2.50 g, 20 mmol) was added dropwise to a stirring solution of 10 mmol of acid in 15 mL of dry CH_2Cl_2 at 35 °C, and the stirring was continued for 2 h. The solution was evaporated under vacuum, and the residual acid chloride was dissolved in 100 mL of dry ether. The solution was added dropwise over a 0.5-h period to a stirring solution of 13 mmol of diazomethane and 10 mmol of distilled triethylamine in 50 mL of anhydrous ether at 0 °C, and the stirring was continued for 2 h. The mixture was filtered, and the filtrate was evaporated. Chromatography of the residue through a short column of neutral alumina (activity III) and elution with 25:1 hexane-ethyl acetate led to the diazo ketone, which was used in the next reaction without further purification.

Diazoacetylcycloheptane (1d): Yellow liquid (85%); IR C=N_2 2100 (s), C=O 1600 (s) cm^{-1}; ^1H NMR δ 1.3-2.5 (m, 13 H), 5.21 (bs, 1 H).

Diazoacetylcyclooctane (1e): Yellow, amorphous solid (66%); IR C=N_2 2100 (s), C=O 1610 (s) cm^{-1}; ^1H NMR δ 1.3-2.5 (m, 15 H), 5.22 (bs, 1 H).

Diazoacetylcyclononane (1f): Yellow, amorphous solid (70%); IR C=N_2 2100 (s), C=O 1600 (s) cm^{-1}; ^1H NMR δ 1.3-2.5 (m, 17 H), 5.23 (bs, 1 H).

1-Diazo-5-cyclohexyl-pentan-2-one (7a): Yellow, amorphous solid (..%); IR C=N 2095 (s), C=O 1615 (s) cm^{-1}; ^1H NMR δ 0.8-1.7 (m, 15 H), 2.31 (t, 2 H, J = 7.0 Hz), 5.21 (bs, 1 H).

1-Diazo-heptan-2-one (7b): Yellow, amorphous solid (68%); IR C=N 2100 (s), C=O 1625 (s) cm^{-1}; ^1H NMR δ 0.91 (t, 3 H, J = 7.0 Hz), 1.2-1.5 (m, 4 H), 1.5-1.8 (m, 2 H), 2.32 (t, 2 H, J = 7.0 Hz), 5.23 (bs, 1 H).

Diazo Ketone Decomposition over Dirhodium Tetraacetate or Dirhodium Tetratrifluoroacetate. A solution of 2 mmol of diazo ketone in 150 mL of CH_2Cl_2 was added dropwise over a 5-h period to a suspension of 0.04 mmol of the catalyst in 50 mL of CH_2Cl_2. The mixture was evaporated under vacuum. Chromatrography of the residue and elution with 30:1 hexane-ethyl acetate yielded the following products.

***Trans*-Bicyclo [8.2.0]dodecan-11-one (5d).** Colourless liquid (25%); IR C=O 1776 (s) cm^{-1}; ^1H NMR δ 1.35-2.28 (m, 17 H), 2.62 (ddd, 1 H, J = 18.0, 6.0, 3.0 Hz), 2.94 (m, 1 H), 3.11 (ddd, 1 H, J = 18.0, 9.0, 3.0 Hz); ^{13}C NMR δ 211.9, 66.3, 51.8, 36.3, 33.5, 27.8, 24-26 (bs). Anal. Calcd for $C_{12}H_{20}O$: C, 79,94; H, 11.18. Found: C, 79.85; H, 11.22.

***Cis*-Bicyclo [7.2.1]dodecan-10-one (6).** Colourless liquid (20%); IR C=O 1740 (s) cm^{-1}; ^1H NMR δ 1.1-2.7 (m, 20 H); ^{13}C NMR δ 217.5, 47.7, 43.2, 34.1, 33.0, 29.3, 26.9, 25.1, 24.5, 23.7. Anal. Calcd for $C_{12}H_{20}O$: C, 79,94; H, 11.18. Found: C, 79.83; H, 11.24.

Ketene Dimer (8a). Colourless liquid (56%); IR C=O 1865 (s), 1725 (s) cm^{-1}; ^1H NMR δ 1.12-1.98 (m, 16 H), 2.27 (sext, 1 H, J = 8.0 Hz), 2.76 (sext, 1 H, J = 9.0 Hz), 3.9 (dd, 1 H, J = 8.0, 1.5 Hz), 4.67 (dd, 1 H, J =

8.0, 1.5 Hz); ^{13}C NMR δ 169.4, 144.2, 106.9, 57.9, 38.1, 36.1, 33.5, 33.4, 29.8, 29.7, 25.1, 25.0. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76,33; H, 9.15. Found: C, 76.41; H, 9.11.

Ketene Dimer (8b). Colourless liquid (68%); IR C=O 1862 (s), 1725 (s) cm^{-1}; ^{1}H NMR δ 1.0-1.8 (m, 21 H), 1.89 (m, 1 H), 2.38 (m, 1 H), 3.79 (dd, 1 H, *J* = 6.0, 1.5 Hz), 4.59 (dd, 1 H, *J* = 9.0, 1.5 Hz); ^{13}C NMR δ 168.9, 143.1, 108.1, 59.5, 36.6, 34.6, 33.3, 33.1, 29.7, 29.6, 25.9, 25.8, 25.7. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77,38; H, 9.74. Found: C, 77.42; H, 9.69.

Ketene Dimer (8c). Colourless liquid (36%); IR C=O 1861 (s), 1726 (s) cm^{-1}; ^{1}H NMR δ 1.2-2.1 (m, 24 H), 2.5 (m, 1 H), 3.82 (dd, 1 H, *J* = 8.0, 1.5 Hz), 4.71 (dd, 1 H, *J* = 10.0, 1.5 Hz); ^{13}C NMR δ 169.2, 142.6, 109.0, 59.96, 38.4, 36.2, 35.2, 35.0, 31.8, 31.2, 28.1, 28.0, 27.7, 26.2, 26.1. Anal. Calcd for $C_{18}H_{28}O_2$: C, 78,21; H, 10.21. Found: C, 78.27; H, 10.17.

***Trans*-Bicyclo[5.2.0]nonan-8-one (5a).** Colourless liquid (10%); IR C=O 1772 (s) cm^{-1}; ^{1}H NMR δ 1.0-2.0 (m, 10 H), 2.12 (m, 1 H), 2.4-3.4 (m, 3 H); ^{13}C NMR δ 207.2, 65.6, 49.3, 34.8, 31.9, 30.5, 30.1, 28.4, 27.7. Anal. Calcd for $C_9H_{14}O$ (mixture of *trans* and *cis* isomers): C, 78,21; H, 10.21. Found: C, 78.28; H, 10.17.

***Cis*-Bicyclo[5.2.0]nonan-8-one (5a).** Colourless liquid (7%); IR C=O 1772 (s) cm^{-1}; ^{1}H NMR δ 1.0-2.0 (m, 10 H), 2.12 (m, 1 H), 2.4-3.4 (m, 3 H); ^{13}C NMR δ 212.6, 63.4, 50.1, 32.6, 29.7, 29.1, 25.6, 25.5, 23.6.

Ketene Dimer (9a). Colourless liquid (30%); IR C=O 1854 (s), 1724 (s) cm^{-1}; ^{1}H NMR δ 1.0-1.95 (m, 34 H), 3.94 (td, 1 H, *J* = 7.0, 1.0 Hz), 4.58 (td, 1 H, *J* = 8.0, 1.0 Hz); ^{13}C NMR δ 169.8, 145.5, 101.7, 53.7, 37.4, 37.3, 36.9, 36.8, 33.4, 33.3, 27.7, 26.7, 26.6, 26.5, 26.4, 26.3, 24.9, 23.6. Anal. Calcd for $C_{22}H_{36}O_2$: C, 79,46; H, 10.91. Found: C, 79.52; H, 10.86.

Ketene Dimer (9b). Colourless liquid (16%); IR C=O 1870 (s), 1730 (s) cm^{-1}; ^{1}H NMR δ 0.8-1.8 (m, 20 H), 2.12 (m, 2 H), 3.92 (td, 1 H, *J* = 7.0, 1.0 Hz) 4.69 (td, 1 H, *J* = 7.0, 1.0 Hz); ^{13}C NMR δ 169.6, 145.6, 101.6, 53.7, 31.2, 31.1, 29.0, 27.4, 25.9, 24.5, 22.3, 22.2, 13.9, 13.8. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74,95; H, 10.78. Found: C, 74.88; H, 10.81.

Ketene Dimer (9c). Colourless liquid (18%); IR C=O 1858 (s), 1728 (s) cm^{-1}; ^{1}H NMR δ 1.2-2.2 (m, 12 H), 2.41 (t, 2 H, *J* = 7.0 Hz), 3.96 (td, 1 H, *J* = 7.0, 1.0 Hz), 4.71 (td, 1 H, *J* = 7.0, 1.0 Hz) 3.9-5.1 (m, 4 H), 5.68-5.92 (m, 2 H); ^{13}C NMR δ 169.4, 138.3, 137.6, 115.3, 114.8, 101.4, 53.7, 33.3, 33.1, 29.7, 28.6, 26.9, 25.5, 24.1. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76,33; H, 9.15. Found: C, 76.40; H, 9.12.

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7. If it be assumed that the carbenoid-rhodium complex interacts with a nucleophile (e.g., water) an adduct [$RC(OH)CH(Rh)N_2^+$] might be formed whose fragmentation would lead to cycloalkanecarboxylic acid (**2**) and a diazomethane-rhodium complex ($RhCHN_2$).
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