Transition Metal Complexes of Diazenes, XL [1]
Iron Carbonyl Assisted Formation of Bicyclic 1,2-Dihydropyrazol-3-ones from Pyrazolines and Alkynes

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The oxidative degradation of a tricyclic dicarbonyl iron complex substituted at the diazaferrole ring by ester groups (1b) does not lead to a bicyclic 1,2,3-diazepinone derivative, as reported recently for the case of the phenyl substituted compound (1a), but affords the bicyclic 4-stilbenyl-1,2-dihydropyrazol-3-one 2b as shown by X-ray structural analysis. Since 1b is obtained by reaction of two different alkynes with a hexacarbonyldiiron complex of the cyclic 1,2-diazene, the over-all reaction formally consists of the addition of CO and two alkylene molecules to an N=N function affording a vinyl substituted diazacyclopentenone ring, and may be viewed as a type of hetero Pauson-Khand reaction.

Introduction

Recently we have reported that the hitherto unknown 1,2,3-diazepinones can be obtained from 1-pyrazolines and alkynes via an iron carbonyl assisted reaction sequence [2,3]. A key step was the oxidative degradation of the tricyclic dicarbonyl iron complex 1a with bromine in the mixed solvent glacial acetic acid-dichloromethane (Scheme 1). The structure of the tetraphenyl substituted derivative 2a was deduced from single crystal X-ray structural analysis [2]. Formation of this product can be rationalized by cleavage of the Fe-CR and Fe-C(R') bonds followed by reductive elimination. From the similarity of IR and NMR data of the dicarbomethoxy-diphenyl substituted compound 2b, the same type of structure was proposed [2]. However, in the mean time single crystals of this compound could be obtained and an X-ray structural investigation showed that 2b has a different structure.

Results and Discussion

The basic structural skeleton of 2b consists of a 1,5-diazaacyclo[3.3.0]cyclooctenone moiety with an angle of 26.3° between the mean planes of the 1,2-dihydropyrazol-3-one ring and C29-N1-N2-C31 (Fig. 1). While the pyrazolone ring is planar (r.m.s.d. 2.8 pm, for all ring atoms N1-O6), the pyrazoline ring is puckered with atom C30 no less than 55.5 pm away from the mean plane C29-N1-N2-C31 (r.m.s.d. 0.1 pm).

The bond lengths within the pyrazolone ring, N1-N2 (137.7 pm), N1-C5 (136.4 pm), C5-C4 (137.3 pm), C4-C3 (146.3 pm), C3-O6 (122.7 pm), and C3-N2 (139.7) are within the expected range and compare well with literature data of monocyclic analogues like 4-bromo-1,2-dihydro-1,5-dimethyl-2-phenyl-3H-pyrazol-3-one [4]. Noteworthy is the approximate coplanar arrangement of the 1,3-dienyl fragment C8-C7-C4-C5-C25 as indicated by the small torsion angles of 4.7 and 7.3° observed for C7-C4-C5-C25 and C19-C7-C8-C13, respectively.

The multistep formation of the pyrazolinone 2b (Scheme 2) [2,3] from the 1-pyrazoline proceeds via complexation (step a), subsequent addition of dimethyl acetylene dicarboxylate and tolan (step b) to afford 1b, followed by oxidative removal of the iron carbonyl group. In its final result it resembles the Pauson-Khand reaction [5]. In this cobalt carbonyl assisted transformation a cyclopentenone is produced from an alkyne, carbon monoxide, and an olefin. In the present case the olefin is replaced by the 1,2-diazene, and participation of two alkyne molecules gives rise to a vinyl substituted diaz-
cyclopentenone. The mechanism of this unprecedented oxidatively induced conversion of 1b into 2b is not known. Rather than a 1,3-migration of the ester group, a nucleophilic attack of the methoxy ester group at the acyl ligand, accompanied by cleavage of ester C-OME and Fe-CO bonds, may be involved.

Experimental

Compound 2b was synthesized according to lit. [2]. Single crystals were obtained from dichloromethane/n-heptane upon standing in an open Erlenmeyer flask at room temperature. The X-ray diffraction data were collected on a Siemens AED automated diffractometer at 298 K, using MoKα radiation (λ = 0.71069 Å). The structure was solved by direct methods (MULTAN-80 program) and refined by the block-matrix least-squares method (SHELX-76 program). The function minimized was Σw(Fo - Fe)², where w⁻¹ = σ²(F). The final cycles of refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms (379 parameters). Positions of hydrogen atoms were calculated on geometrical grounds and kept fixed during the refinement, with Uiso = 0.06 Å². The final difference Fourier map was featureless.
Scheme 2: a) Fe(CO)₅; b) (i) EC₂E, (ii) PhC₂Ph; c) Br₂

C₃₁H₃₂N₂O₉ (2b) (576.60), yellow irregular crystals, crystal size 0.3 x 0.4 x 0.4 mm, triclinic crystal system, space group P1, a = 1612.5(3), b = 1117.2(2), c = 804.7(1) pm, α = 91.76(1), β = 88.54(1), γ = 80.92(1)°, V = 1.4301(4) nm³, d(calc) = 1.339 g/cm³ (Z = 2), μ(MoKα) = 0.925 cm⁻¹. 5426 reflections collected, 5070 unique (Rint = 0.010), 2894 observed with F > 5σ(F); R = 0.039, wR = 0.045, S = 1.448.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary material. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (FAX: Int. code + (1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk)

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[6] For a recent summary of more conventional preparations of 1,2- dihydropyrazol-3-ones see e.g.: L. F. Tietze, A. Steinmetz, Synlett 7, 667 (1996).