Fragmentation and Rearrangement of Carbonyl-bridged Compounds. Synthesis and Crystal Structure of New Spirocycles containing Azetidine Rings

Gabriele Bocelli,[a] G. Paolo Chiusoli,[b]* Mirco Costa,[b] and Luca Fambri[b]

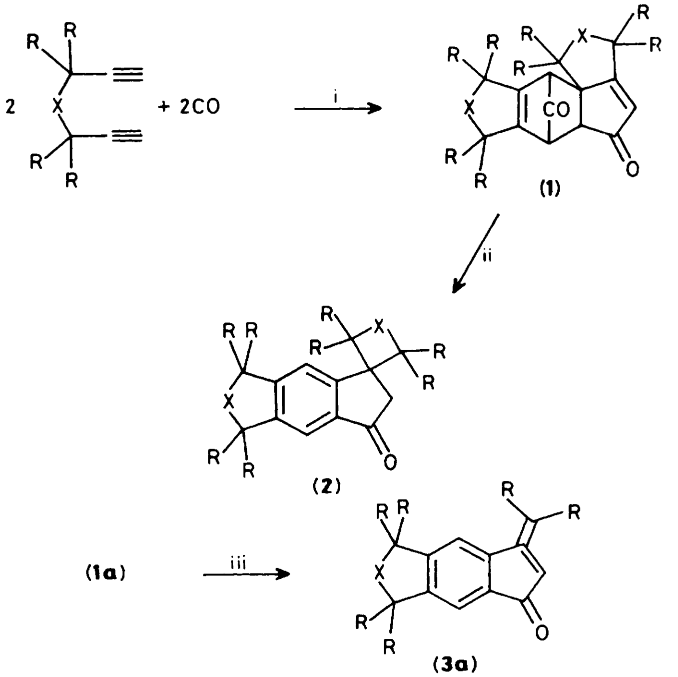
[a] *Centro di Studio per la Strutturistica Diffratometrica del C.N.R., Viale delle Scienze 1, I-43100 Parma, Italy*
[b] *Istituto di Chimica Organica dell'Universita', Viale delle Scienze 1, I-43100 Parma, Italy*

Fragmentation and rearrangement of CO-bridged compounds prepared by carbonylation of alk-1,6-diynes, give rise to new spirocycles, or to tricyclic ketones; the *X*-ray crystal structures of two spirocycles, containing azetidine rings, are reported.

We recently described[1] a simple, high yield synthesis of cyclopentadienone dimers (**1**) from readily available 1,6-diynes and carbon monoxide [X = CH_2, NH, NMe, O; R = H (when X ≠ NH), Me]. When treated with a base such as sodium phenoxide or potassium t-butoxide in dimethoxyethane or other aprotic solvents at room temperature, compounds (**1**) (X = NH, NMe; R = Me) readily decarbonylate and rearrange to (**2**). Thus (**1a**) and (**1b**) give (**2a**) and (**2b**), respectively (*ca.* 80% yield).† Compound (**2**) could also be obtained by thermal treatment of (**1**). Thus compound (**1c**) on heating at 200 °C for 10 min gave the corresponding (**2c**) in 30% yield.‡

Although decarbonylation and aromatization reactions of CO-bridged compounds are well known,[2] such an easy loss of carbon monoxide and the concomitant rearrangement leading to spiro compounds have not been reported previously. Spiro compounds are not readily accessible and the class reported here appears to be a novel one. In particular compound (**2a**) is a new spirocyclic azetidine (m.p. 208—210 °C). *X*-Ray structural investigation§ of this compound, and of its *N*-methyl derivative (**2b**) (m.p. 181—182 °C) prepared in an analogous way, shows that the azetidine ring is approximately perpendicular to the cyclopentane ring although there are significant differences in the dihedral angles at the spiro centre [109.8(2) and 91.7(4)°, respectively], and that it has the form of an envelope with the concavity facing the other part of the molecule. The condensed parts of the molecule are not planar, 4.5(1) and 0.7(5)°, 2.3(5) and 17(5)° being the dihedral angles formed by the central ring plane and the two external five membered ring planes in compounds (**2a**) and (**2b**), respectively. The puckering angles of the four membered rings are 159.5(4) and 155.5(1)° in the two compounds, respectively.

Elution of (**1a**) through a silica gel column with n-hexane–ethyl acetate–methanol (70 : 25 : 5) afforded the corresponding compound (**3a**) in 71% yield. This is another interesting pathway, involving fragmentation and loss of a $Me_2C{=}NH$ group. Thermal treatment of (**1a**) also gives rise to (**3a**) (m.p. 167—168 °C) in lower yield (30%). In this case compound (**3a**) is accompanied by the corresponding (**2a**) (36 : 19 molar ratio) but it does not derive from the latter. A small amount of (**3a**) is also formed in the sodium phenoxide-promoted rearrange-



a; X = NH, R = Me
b; X = NMe, R = Me
c; X = CH_2, R = H

Scheme 1. *Reagents and conditions:* i, Pd/C, room temperature; ii, NaOPh or $KOBu^t$, $MeO(CH_2)_2OMe$, room temperature; iii, SiO_2 column, n-hexane–$MeCO_2Et$–MeOH (70 : 25 : 5).

---

† Yields were determined by g.l.c. with internal standards. All compounds gave satisfactory microanalytical data.

‡ *Selected spectroscopic data* for (**2c**): *m/z* 212 (M^+), 184 (100%), 156; i.r. (KBr), 1700s (CO), 1620m (C=C) cm^{-1}; U.v. (95% EtOH), λ 306.0 (ε 6 000), 256.8 nm (16 000 mol^{-1} dm^3 cm^{-1}); ^1H n.m.r. ($CDCl_3$), δ 2.05—2.19 (m, 4H, cyclobutane symmetric CH_2), 2.20—2.36 (m, 2H, cyclopentane CH_2), 2.43—2.56 (m, 2H, cyclobutane CH_2), 2.88—3.03 (m, 4H, 2 × benzylic CH_2), 2.90 (s, 2H, CH_2CO), 7.48, 7.56 (2 × s, 2H, aromatics); ^{13}C n.m.r. ($CDCl_3$), δ 16.51, 25.87, 32.13, 33.32, 36.30 (5 × t), 44.26 (s), 53.10 (t), 118.21, 119.42 (2 × d), 134.81, 144.31, 153.24, 160.86, 199.81 (5 × s).

(**3a**): *m/z* 269 (M^+), 255, 254 (100%, *M* −Me), 239; i.r. (KBr) 1700s (CO), 1610m (C=C) cm^{-1}; u.v. (95% EtOH), λ 271.5 (ε 22 600), 251.0 nm (37 600 mol^{-1} dm^3 cm^{-1}); ^1H n.m.r. ($CDCl_3$), δ 1.45, 1.50 (2 × s, 12H, 4Me), 1.95, 2.20 (2 × s, 6H, 2Me), 2.35 (br. s, 1H, NH), 3.25 (s, 2H, CH_2), 7.20, 7.55 (2 × s, 2H, aromatics), ^{13}C n.m.r. ($CDCl_3$), δ 21.89, 24.53, 31.86 (3 × q), 43.03, (t), 62.04, 62.59 (2 × s), 116.40, 117.76 (2 × d), 126.0, 130.5, 138.0, 148.7, 150.3, 156.7, 201.69 (7 × s).

§ *Crystal data* for (**2a**): $C_{21}H_{30}N_2O$, $M = 326.48$, monoclinic, space group $P2_1$, $a = 10.474(2)$, $b = 11.458(2)$, $c = 8.384(3)$ Å, $\beta = 104.39(4)°$, $Z = 2$, $D_c = 1.11$ g cm^{-3}, $U = 974.6(5)$ Å^3, Cu-K_α, $\lambda = 1.5418$ Å. Of 2066 collected reflections, 1216 with $I \geqslant 2\sigma(I)$ were considered observed and used in the refinement of the structure solved by direct methods with SHELX.[3] The refinement was carried out by full-matrix anisotropic least-squares to a final *R* of 0.036.

(**2b**): $C_{23}H_{34}N_2O$, $M = 334.53$, monoclinic, space group $P2_1/c$, $a = 12.718(2)$, $b = 14.216(2)$, $c = 11.872(3)$ Å, $\beta = 94.63(3)°$, $Z = 4$, $D_c = 1.10$ g cm^{-3}, $U = 2139.4(7)$ Å^3, Cu-K_α, $\lambda = 1.5418$ Å. 4451 reflections were collected on a Siemens AED single crystal diffractometer in the range θ—2θ. The structure was solved by direct methods with SHELX and refined by anisotropic block-matrix least-squares using 3330 observed reflections at the $3\sigma(I)$ level. The final conventional *R* factor was 0.066.

For both compounds the hydrogens were found on the ΔF map and refined isotropically. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

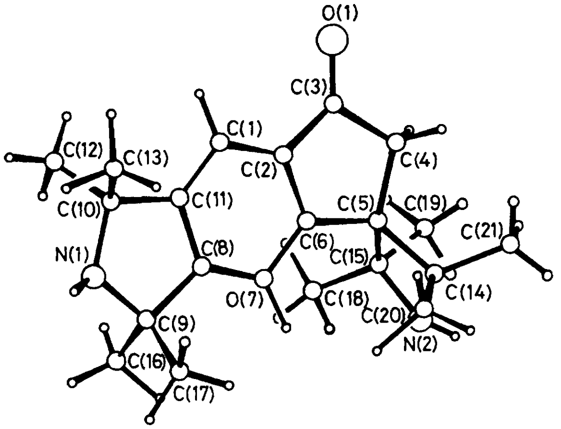


Figure 1. Molecular structure of compound (**2a**). Selected bond distances (Å) and angles (°): C(4)–C(5) 1.550(4), C(5)–C(6) 1.524(3), C(5)–C(14) 1.531(11), C(5)–C(15) 1.651(12), N(2)–C(14) 1.436(10), N(2)–C(15) 1.528(10), N(1)–C(9) 1.479(3), N(1)–C(10) 1.470(4); C(4)–C(5)–C(14) 120.6(4), C(6)–C(5)–C(14) 118.0(3), C(4)–C(5)–C(15) 116.0(3), C(6)–C(5)–C(15) 114.1(3), C(14)–C(5)–C(15) 85.2(4), C(5)–C(14)–N(2) 92.8(5), C(5)–C(15)–N(2) 85.0(5), C(14)–N(2)–C(15) 93.3(4).

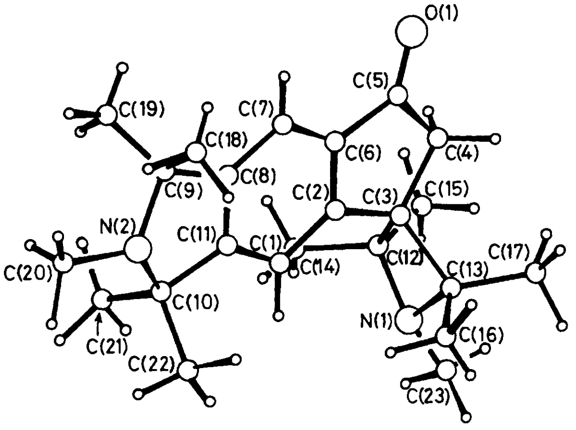


Figure 2. Molecular structure of compound (**2b**). Selected bond distances (Å) and angles (°): C(3)–C(4) 1.541(3), C(2)–C(3) 1.520(2), C(3)–C(12) 1.580(2), C(3)–C(13) 1.584(2), N(1)–C(12) 1.484(3), N(1)–C(13) 1.473(2), N(2)–C(9) 1.471(3), N(2)–C(10) 1.474(2); C(12)–C(3)–C(13) 85.8(1), C(2)–C(3)–C(13) 115.5(1), C(2)–C(3)–C(12) 115.7(1), C(4)–C(3)–C(12) 117.9(2), C(4)–C(3)–C(13) 119.0(1), C(3)–C(12)–N(1) 87.7(2), C(3)–C(13)–N(1) 87.9(1), C(12)–N(1)–C(13) 93.5(1).

ment of (**1a**) to (**2a**) at room temperature. The reaction appears to be sensitive to the nature of X. Formation of (**3**) was not observed with X = CH_2, O.

We thank the National Research Council of Italy and Ministero della Pubblica Istruzione for financial support.

Received, 23rd March 1987; Com. 356

References

1 G. P. Chiusoli, M. Costa, M. Gerbella, and G. Salerno, *Gazz. Chim. Ital.*, 1985, **115**, 697.

2 M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261.

3 G. M. Sheldrick, SHELX, program for crystal structure determination, University of Cambridge, England, 1976.