

Figure 2. Temperature-dependent UV-vis spectra of $(\text{Cl}_2\text{-phen})\text{Co}(\text{3,6-DBBQ})_2$ in toluene solution.

In order to scrutinize the behavior of the cobalt(II) complex at low temperature, electronic spectra (400–820 nm) over the temperature range of 180–300 K were measured in toluene. The spectra of $(\text{Cl}_2\text{-phen})\text{Co}(\text{3,6-DBBQ})_2$ show reversible dependence upon temperature in solution (Figure 2). The band at 790 nm, characteristic of the low spin Co(III) species, decreases at reduced temperatures and is replaced by the transitions at 620 nm which is associated with the high spin Co(II) species.⁶ Thus, the electronic spectra recorded in toluene at temperatures where different tautomeric forms of the complex exist show features that are characteristic of the Co(III) and Co(II) charge distributions. Solution spectra at 210, 240, and 270 K show that at the respective temperature a mixture of Co(III) and Co(II) species exist at equilibrium. The temperature dependence of the solution spectra results from Co(III)/Co(II) transition via an intramolecular cobalt to catechol electron transfer.

In conclusion, the band intensity assigned cobalt to catechol charge transfer is linearly dependent upon Hammett constant of the 4,7-disubstituted 1,10-phenanthroline analogs. For such a bistability system, desirable charge distribution and tautomer equilibria may be anticipated from the Hammett constants. Equilibria between Co(III) and Co(II) tautomers in solution can be also controlled by temperature.

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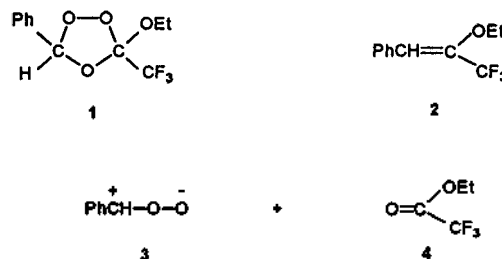
3-Trifluoromethyl-3-Phenyl-5,5-Dialkyl-1,2,4-Trioxolanes by Cross-Ozonolysis Reactions

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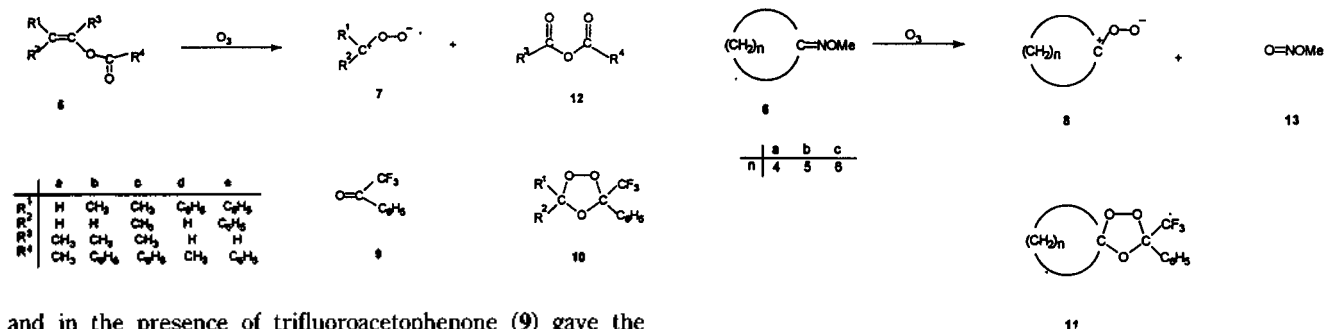
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Ozonides of type 1 which bear trifluoromethyl substituents at the ozonide ring have been unknown until recently when the first representatives were prepared by ozonolyses of trifluoromethyl substituted olefins 2.¹ The formation of ozonides 1 could be explained *via* fragments 3 and 4.²



The fact, that vinylic chlorides,³ vinyl ethers,⁴ vinyl esters⁵ (5) and O-methylated oximes⁶ (6) are cleaved to give acyl chlorides, esters, anhydrides (12) and methyl nitrite (13), respectively, along with the complementary carbonyl oxides, could intimate cleavage of olefin 2 to give fragments 3 and 4 are formed. But the carbonyl oxides (7, 8) and carbonyl compounds (12, 13) do not undergo [3+2]-cycloadditions to give ozonides. The failure to afford the corresponding ozonides has been attributed to the low reactivity of the ensuing carbonyl compounds. In this paper we have tried to prepare trifluoromethyl substituted ozonides by reactions of more reactive trifluoroacetone (9) with carbonyl oxides (7, 8) which are generated from sources other than parent olefins 2, *viz.* by ozonolysis of enol esters 5 and O-methylated oximes 6.^{7,8} The method described here has the advantage that the enol ester 5 and the O-methyl oximes 6 are readily accessible from the corresponding carbonyl compounds.

Ozonolyses of the enol ester 5a-e in pentane at $-78\text{ }^\circ\text{C}$



and in the presence of trifluoroacetophenone (9) gave the corresponding ozonides **10a-e**. They were isolated in yields of 22% to 43% and characterized by their ¹H- and ¹³C NMR spectra.

At room temperature and ozonides were stable when they are isolated as solids, whereas the liquid ozonides **10** underwent gradual decomposition. Ozonides **10b** and **10d** were mixtures of two stereoisomers, which could be isolated separately in each case. The stereoisomers have been tentatively assigned on the assumption that, as in other reported cases, the ¹H NMR signal of the hydrogen attached two the ozonide ring appears in a higher field position for the trans-isomer than for the cis-isomer.⁹

Stereochemistry of the solid ozonide **10e** was assigned by X-ray analysis.¹⁰ The result of the X-ray analysis is illustrated by Figure 1 together with the numbering system adopted. With respect to the five-membered trioxolane ring, it has a bond length of 1.463(7) Å for the O(1)-O(2) bond and of 1.418(7)-1.461(9) Å for the C-O bonds with puckering carbon angles within the range of 100.7(5)-106.5(5)°, which resulted in similar data as those reported by Kuczowski *et al.*,¹¹ from their study by the microwave spectroscopy. The trioxolane ring adopt an oxygen-oxygen half chair (1) conformation. The O(1) atom, which is located on the apex of a triangular plane of C(2)-O(1)-O(2) is 0.656 Å upward from the molecular plane in the angle of 134° between two planes.

Two benzene rings (2) and (3), which are located above the molecular plane of the trioxolane, have dihedral angles of 106.6°.

Reduction of ozonides **10** with triphenyl phosphine gave *ca.* equimolar amounts of the corresponding fragment **9** and **12**.

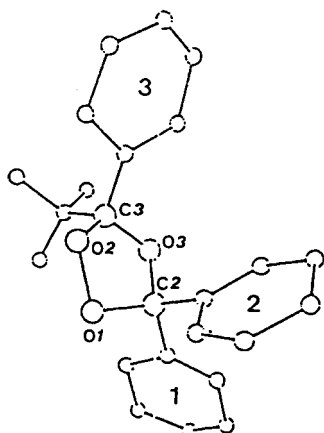
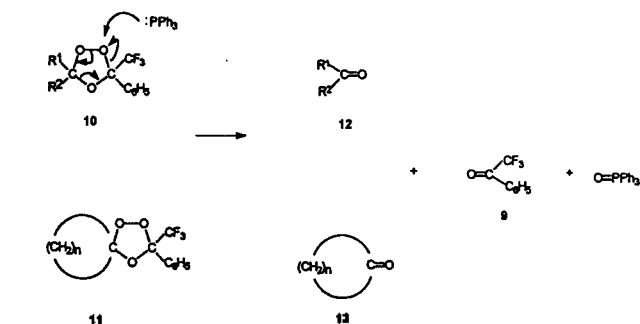


Figure 1. Molecular conformation of ozonide **10e** with the atomic labelling.



Ozonolyses of the *O*-methylated oximes **6** in pentane and in the presence of trifluoroacetophenone gave the corresponding cross ozonides **11**.

The ozonide were isolated in yields between 30% and 50% and characterized by their ¹H and ¹³C NMR spectra. At room temperature the ozonides were proved to be stable compounds. Reduction of ozonides **11** with triphenylphosphine gave corresponding fragments **9** and **13** in approximately equimolar amounts. Since *O*-methylated oximes are more readily accessible than enol esters, we have found this method to be convenient access to ozonides by cross ozonolysis reactions of *O*-methylated oximes and dipolarophiles bearing carbonyl groups.

Experimental

All NMR spectra were recorded with Bruker FT-NMR (200 MHz) and Varian Gemini FT-NMR (300 MHz), using TMS as internal reference for the ¹H- and ¹³C NMR spectra.

Substrates **5a-e**^{12,13} and **6a-c**⁶ were prepared according to published procedures.

Ozonolysis Reactions of enol ester. A *n*-pentane solution of an enol ester and 2,2,2-trifluoroacetophenone in a molar ratio of 1:2 was treated with ozone at -78 °C until the enol ester was consumed. The solution was flushed with nitrogen at room temperature until residual ozone had disappeared and subsequently concentrated by distillation of the solvent at room temperature and reduced pressure. From the residue, the ozonide was isolated by flash chromatography, using 80 g of silica gel and *n*-pentane/diethyl ether in a ratio of 4:1 for ozonide **10a-e**.

Reduction of Ozonides with Triphenylphosphine.

A solution of the ozonide in CDCl₃ was mixed with triphenylphosphine in an NMR tube, and the reaction was monitored by ¹H- and ¹³C NMR spectroscopy.

3-Trifluoromethyl-3-phenyl-1,2,4-trioxolane (10a).

Ozonolysis of 0.2 g (2 mmol) of isopropenyl acetate and

0.67 g (4 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a colorless liquid mixture from which 0.31 g (1.42 mmol, 71%) of 3-trifluoromethyl-3-phenyl-1,2,4-trioxolane (**10a**) was isolated. Colorless liquid; ^1H NMR (CDCl_3) δ (ppm) 5.20 (s, 2H), 5.55 (s, 2H), 7.45-7.68 (m, 5H); ^{13}C (BB)-NMR (CDCl_3) δ (ppm) 96.08, 103.64 (q, $J=17$ Hz), 122.23 (q, $J=287$ Hz, CF_3), 126.97-131.68; $\text{C}_9\text{H}_7\text{O}_3\text{F}_3$ (220.1) calcd. C 49.11, H 3.21; found C 47.56, H 3.27. -Reduction of **10a**. ^1H NMR (CDCl_3) δ (ppm) 7.43-7.99 (m, 5H) for **12a**.

Cis and trans-3-Trifluoromethyl-5-methyl-3-phenyl-1,2,4-trioxolane (10b). Ozonolysis of 0.34 g (2 mmol) of 2-benzoyl-2-butene and 0.67 g (4 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a colorless liquid mixture from which 0.26 g (1.14 mmol, 57%) of a mixture of the stereoisomers of 3-trifluoromethyl-3-phenyl-1,2,4-trioxolane was isolated. By additional separation of this mixture one obtained *cis*-**10b** and *trans*-**10b**.

cis-**10b**: Colorless liquid; ^1H NMR (CDCl_3) δ 6.42 (q, 1H), 1.46 (d, 3H), 7.31-7.70 (m, 5H); ^{13}C NMR δ 14.18-104.21 (q, $J=30$ Hz), 106.83, 128.62 (q, $J=289$ Hz), 124.70-131.66; $\text{C}_{15}\text{H}_{11}\text{O}_3\text{F}_3$ (296.2) calcd. C 60.82, H 3.74; found C 61.05, H 3.81.

trans-**10b**: Colorless liquid; ^1H NMR (CDCl_3) δ 6.09 (q, 1H), 1.59 (d, 3H), 7.31-7.70 (m, 5H); ^{13}C NMR (CDCl_3) δ 15.88-104.21 (q, $J=30$ Hz), 105.69, 128.62 (q, $J=289$ Hz), 124.70-131.66; $\text{C}_{15}\text{H}_{11}\text{O}_3\text{F}_3$ (296.2) calcd. C 60.82, H 3.74; found C 60.08, H 3.68. -Reduction of *cis* and *trans*-**10b**. ^1H NMR (CDCl_3); δ (ppm) 2.17 (d, 3H, $J=2.86$ Hz), 7.43-7.99 (m, 5H), 9.76 (q, 1H, $J=2.90$ Hz) for **12b**.

3-Trifluoromethyl-5,5-dimethyl-3-phenyl-1,2,4-trioxolane (10c). Ozonolysis of 0.57 g (3 mmol) of 2-benzoyl-3-methyl-2-butene and 1.04 g (6 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a colorless liquid mixture from which 0.55 g (2.22 mmol, 74%) of 3-Trifluoromethyl-5,5-dimethyl-3-phenyl-1,2,4-trioxolane (**10c**) was isolated.

Colorless liquid; ^1H NMR (CDCl_3) δ (ppm) 1.39 (s, 3H), 1.65 (s, 3H), 7.39-7.59 (m, 5H); ^{13}C (BB)-NMR (CDCl_3) (ppm) 22.01, 24.79, 104.08 (q, $J=33$ Hz), 112.77, 122.29 (q, $J=290$ Hz, CF_3), 126.64-132.45; $\text{C}_{11}\text{H}_{11}\text{O}_3\text{F}_3$ (248.2) calcd. C 53.23 H 4.47; found C 52.46, H 4.15. -Reduction of **10c**. ^1H NMR (CDCl_3) δ (ppm) 2.09 (s, 6H), 7.43-7.99 (m, 5H) for **12c**.

3-Trifluoromethyl-3,5-diphenyl-1,2,4-trioxolane (10d). Ozonolysis of 0.32 g (2 mmol) of 1-acetoxy-2-phenylethene and 0.67 g (4 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a colorless liquid mixture from which 0.42 g (1.42 mmol, 71%) of 3-trifluoromethyl-3,5-diphenyl-1,2,4-trioxolane (**10d**) was isolated. By additional separation of this mixture one obtained *cis*-**10d** and *trans*-**10d**.

cis-**10d**: Colorless liquid; ^1H NMR (CDCl_3) δ 6.09 (s, 1H), 7.31 (m, 10H); ^{13}C NMR (CDCl_3) δ 104.21 (q, $J=30$ Hz), 106.83, 128.62 (q, $J=289$ Hz), 124.70-131.66; $\text{C}_{15}\text{H}_{11}\text{O}_3\text{F}_3$ (296.2) calcd. C 60.82, H 3.74; found C 61.05, H 3.81.

trans-**10d**: Colorless liquid; ^1H NMR (CDCl_3) δ 6.09 (s, 1H), 7.31 (m, 10H); ^{13}C NMR (CDCl_3) δ 104.21 (q, $J=30$ Hz), 105.69, 128.62 (q, $J=288$ Hz), 124.70-131.66; $\text{C}_{15}\text{H}_{11}\text{O}_3\text{F}_3$ calcd. C 60.82, H 3.74; found C 60.08, H 3.68. -Reduction of **10d**. ^1H NMR (CDCl_3) δ (ppm) 7.43-7.99, 9.98 (s, 1H) for **12d**.

3-Trifluoromethyl-3,5,5-triphenyl-1,2,4-trioxolane (10e). Ozonolysis of 0.47 g (2 mmol) of 1-acetoxy-2-diphenylethene and 0.67 g (4 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a crystalline mixture from which 0.50 g (1.36 mmol, 68%) of 3-trifluoromethyl-3,5,5-triphenyl-1,2,4-trioxolane (**10e**) was isolated. Colorless crystal; ^1H NMR (CDCl_3) δ (ppm) 7.19-7.52 (m, 15H); ^{13}C (BB)-NMR (CDCl_3) δ (ppm) 105.02 (q, $J=33$ Hz), 113.30, 121.67 (q, $J=289$ Hz, CF_3), 126.78, 138.27; $\text{C}_{21}\text{H}_{15}\text{O}_3\text{F}_3$ (372.3) calcd. C 67.75, H 4.06; found C 68.06, H 4.49. -Reduction of **10e**. ^{13}C NMR (CDCl_3) δ (ppm) 116.96 (q, $J=289$ Hz), 128.54-137.91, 180.75 (q, $J=35$ Hz), 196.93 for **12e**.

Ozonolysis Reactions of O-methyl oximes. A *n*-pentane solution of a *O*-methyloxime and of 2,2,2-trifluoroacetophenone in a molar ratio of 1:2 was treated with ozone at 0 °C until the *O*-methyloxime was consumed. The solution was flushed with nitrogen at room temperature until residual ozone had disappeared and subsequently concentrated by distillation of the solvent at room temperature and reduced pressure. From the residue, the ozonide was isolated by flash chromatography, using 80 g of silica gel and *n*-pentane/diethyl ether in a ratio of 4:1 for ozonides **11a-c**.

Reactions of Ozonides with Triphenylphosphine.

A solution of the ozonide in CDCl_3 was mixed with triphenylphosphine in an NMR tube, and the reaction was monitored by ^1H NMR spectroscopy.

3-Trifluoromethyl-3-phenyl-1,2,4-trioxaspiro[4,4]nonane (11a). Ozonolysis of 0.45 g (4 mmol) of cyclohexanone *O*-methyloxime and 1.04 g (6 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a colorless liquid mixture from which 0.44 g (1.61 mmol, 40%) of 3-trifluoromethyl-3-phenyl-1,2,4-trioxaspiro[4,4]nonane (**11a**) was isolated. Colorless liquid; ^1H NMR (CDCl_3) δ (ppm) 1.71-2.22 (m, 8H), 7.40-7.58 (m, 5H); ^{13}C (BB)-NMR (CDCl_3) δ (ppm) 23.46, 24.24, 32.27, 36.40, 103.75 (q, $J=33$ Hz), 122.28, 122.31 (q, $J=290$ Hz, CF_3), 127.21-132.29; $\text{C}_{13}\text{H}_{13}\text{O}_3\text{F}_3$ (274.2) calcd. C 56.94 H 4.78; found C 55.74 H 4.41. -Reduction of **11a**. ^1H NMR (CDCl_3) δ (ppm) 1.91-1.94 (m, 4H), 2.11-2.14 (m, 4H) 7.43-7.99 (m, 5H) for **13a**.

3-Trifluoromethyl-3-phenyl-1,2,4-trioxaspiro[5,4]decane (11b). Ozonolysis of 0.38 g (3 mmol) of cyclohexanone *O*-methyloxime and 1.04 g (6 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a colorless liquid mixture from which 0.61 g (2.66 mmol, 89%) of 3-trifluoromethyl-3-phenyl-1,2,4-trioxaspiro[5,4]decane (**11b**) was isolated. Colorless liquid; ^1H NMR (CDCl_3) δ (ppm) 1.46-1.98 (m, 10H), 7.25-7.55 (m, 5H); ^{13}C (BB)-NMR (CDCl_3) δ (ppm) 23.51, 24.05, 24.83 31.95, 34.10, 103.70 (q, $J=33$ Hz), 113.55, 122.17 (q, $J=290$ Hz, CF_3), 127.13-332.63; $\text{C}_{14}\text{H}_{15}\text{O}_3\text{F}_3$ (288.3) calcd. C 58.33, H 5.24; found C 58.26, H 5.52. -Reduction of **11b**. ^1H NMR (CDCl_3) δ (ppm) 1.69-1.72 (m, 2H), 1.82-1.87 (m, 4H), 2.03~2.33 (m, 4H), 7.43-7.99 (m, 5H) for **13b**.

3-Trifluoromethyl-3-phenyl-1,2,4-trioxaspiro[6,4]undecane (11c). Ozonolysis of 0.42 g (3 mmol) of cycloheptanone *O*-methyloxime and 0.78 g (4.5 mmol) of 2,2,2-trifluoroacetophenone in 50 mL of *n*-pentane according to the general procedure described above gave a crystalline mixture

from which 0.49 g (1.62 mmol, 54%) of 3-trifluoromethyl-3-phenyl-1,2,4-trioxaspiro[6,4]-undecane (**11c**) was isolated. Colorless crystals: $^1\text{H NMR}$ (CDCl_3) δ (ppm) 1.51-2.19 (m, 12H), 7.25-7.58 (m, 5H); ^{13}C (BB)-NMR (CDCl_3) δ (ppm) 22.38, 22.85, 29.48, 29.52, 35.07, 36.78, 103.83 (q, $J=33$ Hz), 117.85, 122.17 (q, $J=290$ Hz, CF_3), 127.14-132.54; $\text{C}_{15}\text{H}_{17}\text{O}_3\text{F}_3$ (302.3) calcd. C 59.60, H 5.67; found C 59.02, H 6.12. -Reduction of **11c**. $^1\text{H NMR}$ (CDCl_3) δ (ppm) 1.64-1.70 (m, 8H), 2.45-2.48 (m, 4H), 7.43-7.99 (m, 5H) for **13c**.

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