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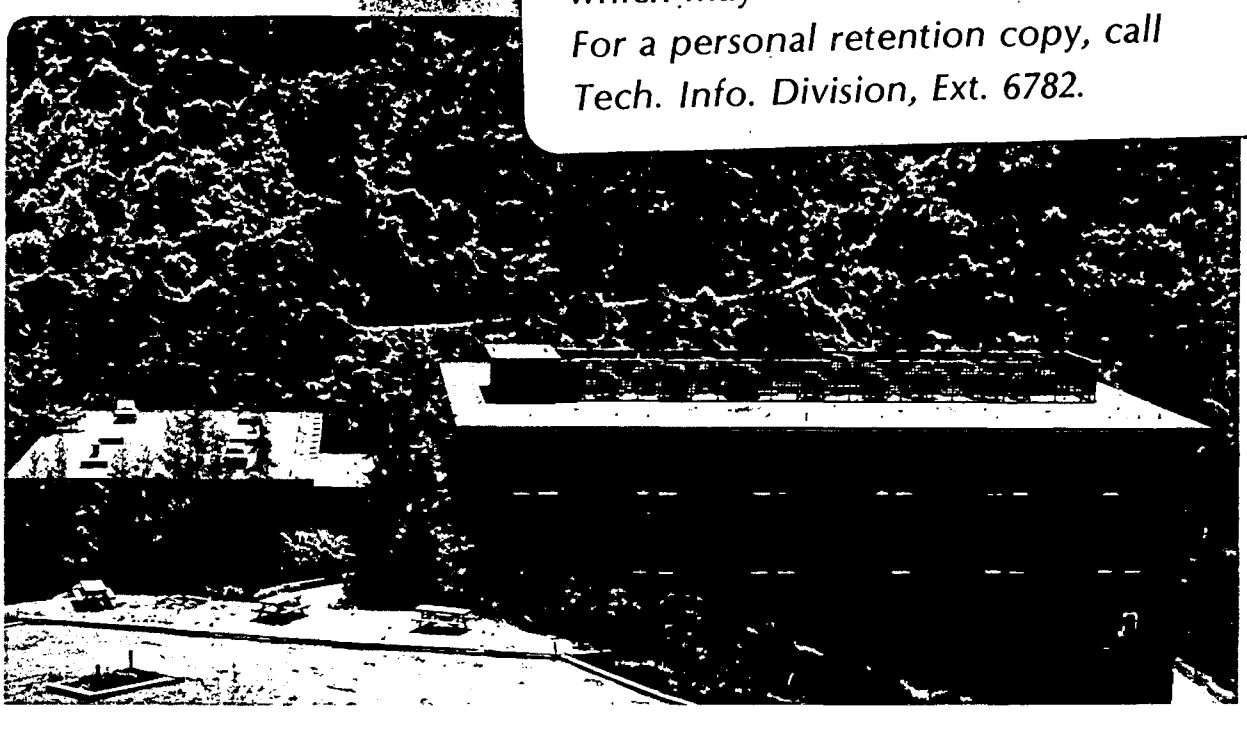

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Thermal Extrusion of Sulfur Dioxide from $(\eta^5\text{-}C_5H_5)Co\text{-}\eta^4$-thiophene-1,1-dioxides: A New Organometallic Reaction

James S. Drage and K. Peter C. Vollhardt*

Department of Chemistry, University of California, and
the Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720

Summary: Flash vacuum pyrolysis of several $(\eta^5\text{-}C_5H_5)Co\text{-}\eta^4$-thiophene-1,1-dioxides leads to extrusion of SO_2 and the formation of $(\eta^5\text{-}C_5H_5)Co\text{-}\eta^4$-cyclobutadiene complexes. Stereochemical labeling experiments have been employed to pinpoint a likely pathway for this new transformation.

Abstract (for Chemical Abstracts)

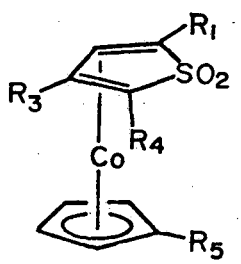
CpCo-η^4-2,5-dimethylthiophene-1,1-dioxide **1** was prepared by irradiation of the free heterocycle in the presence of $CpCo(CO)_2$. Flash vacuum pyrolysis leads solely to CpCo-η^4-1,2-dimethylcyclobutadiene **2** by SO_2 extrusion. A crossover experiment has ascertained that the complexes stay intact during this transformation, ligand exchange cannot be observed. Positional isomerization of the cyclobutadiene ligand (as reported earlier) occurs at higher temperatures than those required to eject SO_2 from its precursor. Pyrolysis of either of the diastereomers of CpCo-η^4-(2-methyl-5-*sec*-butyl)thiophene-1,1-dioxide **9** gave completely diastereoisomerized CpCo-cyclobutadienes **10**, but only partially equilibrated starting materials. The observed data suggest as a reasonable mechanism metal insertion into the thiophene ring followed by SO_2 extrusion involving a deinsertion pathway.

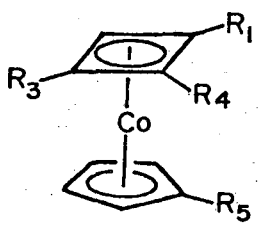
The prospect of increasing utilization of coal and coal-derived liquids as a source of fuel and chemical feed stocks has renewed interest in the development of chemical means by which sulfur may be removed from coal[1]. A large proportion of the organically bound sulfur in coal occurs in the form of thiophene and its derivatives. A potential way of eliminating its presence from such structures would be by an oxidation-thermal desulfonation sequence. Thus, flash vacuum pyrolysis (FVP) of thiophene-1,1-dioxides derived from oxidation of the corresponding thiophenes leads to the predominant formation of furans by presumed loss of "SO"[2].

We have been interested in effecting transition metal mediated SO_2 extrusions from such systems in an effort to ultimately find catalytic organometallic pathways by which thiophene units may be converted into desulfurized chemicals. A previous thermal reactivity study[2a] of an iron tricarbonyl complexed thiophene dioxide was rendered inconclusive due to extensive decomposition and metal deposition, most likely a result of the relatively weak Fe-CO bond. We have previously established the utility of the remarkable thermal stability[3] of the CpCo-unit ($Cp=\eta^5-C_5H_5$) in studies aimed at discovering novel ligand reorganizations[4]. It therefore appeared promising to extend this work to the thermal chemistry of CpCo-thiophene dioxides. This report details the first observation of the elusive[2a] SO_2 extrusion

from such complexes and describes experiments, the outcome of which has considerably narrowed the number of alternatives by which this transformation occurs.

CpCo-η^4-2,5-dimethylthiophene-1,1-dioxide 1 was prepared from $CpCo(CO)_2$ and the free heterocycle[5] by irradiation in boiling benzene (84%)[6]. In solution the compound is stable to





1: $R_1=R_4=CH_3$; $R_3=R_5=H$
2: $R_1=R_4=CH_3$; $R_3=R_5=H$
4: $R_1=R_3=CH_3$; $R_4=R_5=H$
3: $R_1=R_3=CH_3$; $R_4=R_5=H$
5: $R_1=R_4=R_5=CH_3$; $R_3=H$
7: $R_1=R_4=R_5=CH_3$; $R_3=H$
6: $R_1=CH_3CH_2$; $R_4=CH_3$; $R_3=R_5=H$
8: $R_1=CH_3CH_2$; $R_4=CH_3$; $R_3=R_5=H$
9: $R_1=CH_3CH_2CH(CH_3)$; $R_4=CH_3$; $R_3=R_5=H$
10: $R_1=CH_3CH_2CH(CH_3)$; $R_4=CH_3$; $R_3=R_5=H$

light (medium pressure Hg lamp), but unstable when heated beyond 200°C to give intractable tars. In contrast, under flash vacuum pyrolytic conditions[4] (10^{-4} torr, 575°C), 1 is converted to the cyclobutadiene complex 2[6] as the only isolable product (50% isolated yield). Some decomposition is responsible for the formation

of a cobalt mirror in the hot zone of the pyrolysis tube. In addition, a small amount (4%) of starting material is recovered. The mass spectral fragmentation pattern[7] of 2, and particularly the negligible coupling (< 1Hz) between the cyclobutadiene protons[4a,8] (measured in the ^{13}C-satellite ^{1}H-NMR spectrum), clearly showed the presence of the 1,2-disubstitution pattern in the four ring indicating the occurrence of SO_2 extrusion and ligand-bond formation without concomitant rearrangement. However, 2 could be equilibrated with its 1,3-dimethylcyclobutadiene isomer 3 ($J_{H_2H_4}$ = 9Hz)[6] at temperatures above 620°C. Compound 3 was independently prepared by SO_2-extrusion from complex 4 (51%)[6], in turn synthesized in the same way as 1 (97%). We have shown that such isomerizations (e.g. 2⇄3) proceed through retrocyclization of the four-ring to bisalkyne complexes capable of rotation and ring closure[4 b,d], and it is significant that the SO_2 extrusion reaction from 1 or 4 does not enter that manifold at the (lower) temperatures employed.

That the two ligands stay attached to the metal during SO_2 elimination was ascertained through a crossover experiment involving a 1:1 mixture of the (η^5-$CH_3C_5H_4$)Co and η^4-2-ethyl-5-methylthiophene-1,1-dioxide[9] analogs of 1, complexes 5 and 6[6]. FVP (579°C, 10^{-4}torr) gave equimolar amounts of the cyclobutadienes 7 and 8 (40%), in addition to starting materials (15%), but no sign of ligand crossover in any of the recovered complexes (m/e; ^{1}H-NMR).

Among the variety of mechanisms which may be envisaged to describe the loss of SO_2 from complexes 1 and 4-6, the four most reasonable are pictured on Scheme I. Pathway a constitutes a concerted loss of SO_2 from A, an "organometallic" cheletropic extrusion reminiscent of that observed in its organic equivalent, the loss of SO_2 from 2,5-dihydrothiophene-1,1-dioxides[10], but involving simultaneous C-C bond formation. In contrast, b proposes a concerted retrocyclization of A to SO_2 and a bisalkyne complex B which would readily close[4b] to product, most likely through the intermediacy of a metallacyclopentadiene of the type C[11]. The latter might also be directly accessible via c, this route possibly involving SO_2 expulsion from a valence tautomer of A in which the metal is bound in an η^2-manner to the ligand at C-2 and C-5. Finally, pathway d suggests an insertion into the C-SO_2 bond to give D, followed by SO_2 loss, most likely involving complex E, and then C. The last sequence is superficially related to the extensively investigated SO_2 insertion-deinsertion reactions into metal alkyls[12].

Information with respect to the relative likelihood with which each of these mechanisms (or their topological equivalents) might occur may be obtained by a stereochemical labeling experiment. Thus, introduction of two different substituents at C-2 and C-5, one of which is chiral, (as indicated in A, Scheme I), gives rise to diastereomers, the stereochemical (non)integrity of which during FVP would be of interest. With this thought in mind the two isomers of CpCo (2-methyl-5-sec-butyl-thiophene-1,1-dioxide) 9a,b were prepared[13] (1:1 mixture) and separated by h.p.l.c. (silica gel, $CHCl_3$)[6].

The results of the pyrolyses of each isomer are shown in Table I.

It is evident that the product cyclobutadienes 10a,b[6] are completely diastereoisomerized, while the starting material is recovered only partially diastereoisomerized. This finding in

SCHEME I

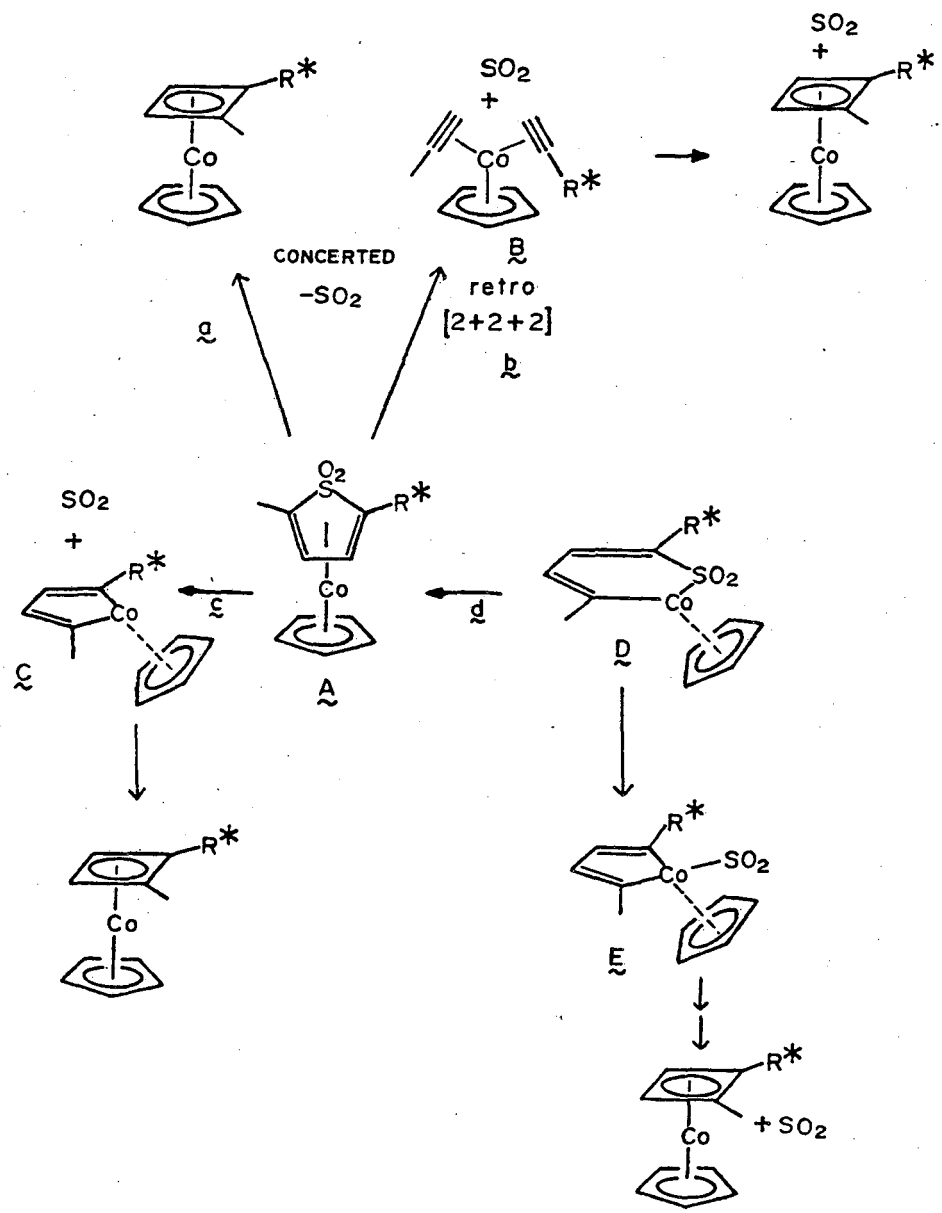


Table I. Results of the FVP of 9a and 9b

Starting Material	Pyrolysis Temperature (°C)	9a:9b (% yield)	10a:10b (% yield)
9a	507	87:13 (72)	50:50 (18)
	541	79:21 (37)	50:50 (36)
	575	75:25 (4)	50:50 (49)
9b	510	15:85 (70)	50:50 (18)
	540	20:80 (36)	50:50 (34)
	577	25:75 (5)	50:50 (52)

conjunction with the absence of positional isomerization in product as well as starting materials narrows any available mechanistic options. Path a should have generated only one product isomer, path b would have necessitated positional isomerization. Path c requires configurational nonintegrity around the metal in C, a possibility made unlikely by earlier results[4b]. Thus, although by no means proven to be correct, d is left as the currently most appealing mechanistic candidate, involving the postulate of the reversible generation of a configurationally unstable (and rapidly disastereoisomerizing) initial intermediate D, providing the rationale for both stereochemical observations. The reason for the contrasting barriers to inversion at cobalt in C versus D might be attributed to the presumed "anti-aromatic" transition state involved when isomerizing the former. Further mechanistic and theoretical work is in order to clarify these points.

Nevertheless, and in summary, we have uncovered a new organometallic reaction which is likely to proceed through novel organometallic intermediates. These findings might be of some stimulus to mechanistic and synthetic chemists in general, and those interested in particular in sulfur removal from thiophenic contaminents of industrial liquids.

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(6) All new compounds isolated gave satisfactory analytical and/or spectral data. The following compounds are representative:

1: orange crystals; mp 188-190°C; m/e (relative intensity) 268 (M^+, 46), 204 (21), 189 (18), 124 (100); NMR (90 MHz, $CDCl_3$) δ5.00 (s, 2H), 4.90 (s, 5H), 1.70 (s, 6H). 2: yellow oil; m/e (relative intensity) 204.0355 (calcd 204.0349, M^+, 62.7), 189 (19.5), 178 (5.9), 124(100); NMR (90 MHz, $CDCl_3$) δ4.65 (s, 5H), 3.62 (s, 2H), 1.60 (s, 6H). 3: yellow oil; m/e (relative intensity) 204.0341 (calcd 204.0349, M^+, 56.4), 164 (25.7), 124 (100); NMR (200 MHz, $CDCl_3$) δ4.74 (s, 5H), 3.82 (s, 2H), 1.51 (s, 6H). 4: orange oil; m/e (relative intensity) 267.9963 (calcd 267.9968, M^+, 25), 204

(11.8), 124 (100). 9a: orange oil; m/e (relative intensity) 310.0439 (calcd 310.0437, M^+, 53.6), 246 (5.5), 124 (100); NMR (250 MHz, $CDCl_3$) δ5.02 (d, J=3.8, 1H), 4.99 (d, J = 3.8, 1H), 4.92 (s, 5H), 2.37 (m, 1H), 1.88 (m, 1H), 1.60 (s, 3H), 1.52 (m, 1H), 1.06 (d, J = 7.0, 3H), 0.90 (t, J = 7.4, 3H). 9b: orange oil; m/e (relative intensity) 310.0437 (calcd 310.0437, M^+, 56.6), 246 (5.2), 124 (100); NMR (250 MHz, $CDCl_3$) δ5.00 (s, 2H), 4.94 (s, 5H), 2.02 (m, 1H), 1.75 (m, 1H), 1.59 (s, 3H), 1.37 (m, 1H), 1.35 (d, J = 7.0, 3H), 0.95 (t, J = 7.4, 3H). 10a + 10b (inseparable): yellow oil; m/e (relative intensity) 246.0817 (calcd 246.0818, M^+, 74.3), 124 (100); NMR (250 MHz, $CDCl_3$) δ4.78 (s, 5H), 4.77 (s, 5H), 3.74 (s, 1H), 3.72 (s, 1H), 3.61 (s, 1H), 3.60 (s, 1H), 2.04-1.83 (m, 2H), 1.58 (s, 3H), 1.56 (s, 3H), 1.43-1.15 (m, 4H), 1.02 (d, J = 5.0, 3H), 1.00 (d, J = 5.0, 3H), 0.87 (t, J = 7.6, 3H), 0.83 (t, J = 7.6, 3H).

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9. Prepared[6] as follows from 2-methyltiophene: (a) $CH_3COCl,SnCl_4$ (64%); (b) $H_2NNH_2 \cdot H_2O$, KOH, Δ (36%); (c) MCPBA-CH_2Cl_2 (44%); (d) $CpCo(CO)_2$, C_6H_6, Δ, hν (86.5%).
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13. From 2-methylthiophene as follows: (a) CH_3COCl, $SnCl_4$ (64%); (b) CH_3CH_2MgBr, ether (78%); (c) $NaCNBH_3$, HCl, CH_3OH (95%); see: J. S. Drage, R. E. Earl, and K.P.C. Vollhardt, J. Heterocycl. Chem., 19, 0000 (1982); (d) MCPBA-CH_2Cl_2 (25%); (e) $CpCo(CO)_2$, C_6H_6, Δ, $h\nu$ (95%).

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