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Preliminary communication

INSERTION OF *N*-SULFINYLSULFONAMIDES AND BIS(METHYLSULFONYL)SULFUR DIIMIDE INTO IRON—CARBON σ BONDS

ROLAND G. SEVERSON and ANDREW WOJCICKI*

The McPherson Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

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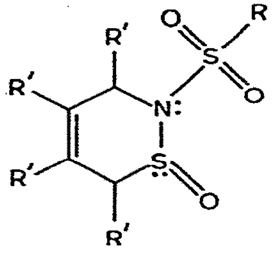
Summary

The *N*-sulfinylsulfonamides $R'S(O)_2N{=}S{=}O$ ($R' = CH_3$, p-$CH_3C_6H_4$) insert into the Fe—R bonds of η^5-$C_5H_5Fe(CO)_2R$ ($R = CH_3$, $CH_2C_6H_5$) to afford η^5-$C_5H_5Fe(CO)_2N[S(O)_2R'][S(O)R]$. These products undergo oxidation by m-$ClC_6H_4C(O)OOH$ to η^5-$C_5H_5Fe(CO)_2N[S(O)_2R'][S(O)_2R]$ and rearrange on storage to η^5-$C_5H_5Fe(CO)_2S(O)[NS(O)_2R']R$. Reaction between the η^5-$C_5H_5Fe(CO)_2R$ and $CH_3S(O)_2N{=}S{=}NS(O)_2CH_3$ leads to the insertion products η^5-$C_5H_5Fe(CO)_2N[S(O)_2CH_3][S(R)NS(O)_2CH_3]$.

The compounds with cumulated double bonds *N*-sulfinylamines, $RN{=}S{=}O$, and sulfur diimides, $RN{=}S{=}NR$, may be regarded as close electronic and structural analogues of sulfur dioxide. This analogy is reflected in several aspects of their organic chemistry, e.g., cycloaddition reactions [1—3], as well as in their ability to form transition metal complexes [4—6]. Reported here is a further extension of the comparative chemistry of these cumulenes, namely their behavior toward transition metal—carbon σ bonds. Insertion of SO_2 into metal—carbon linkages is a well known reaction [7].

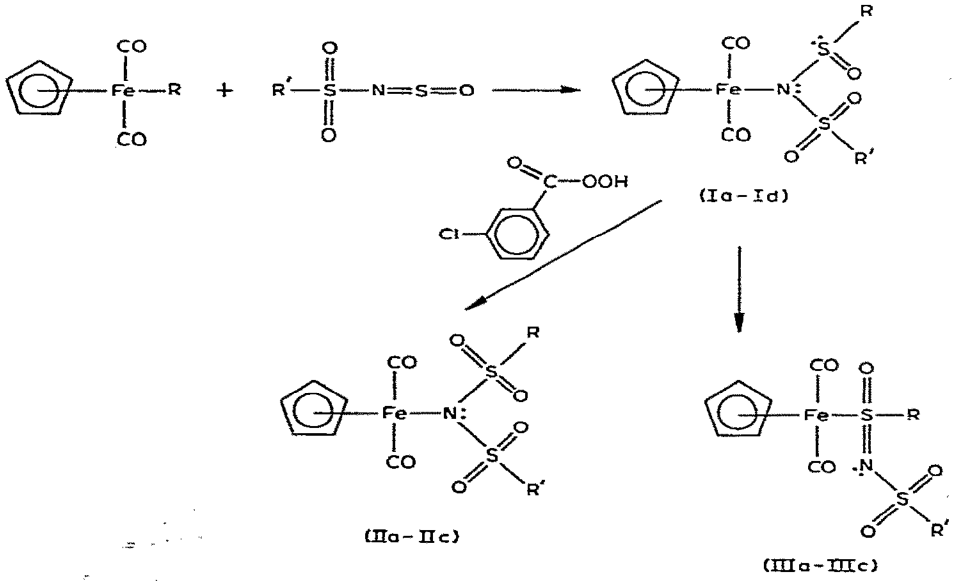
Although there is no detectable interaction between η^5-$C_5H_5Fe(CO)_2CH_3$ and each of $C_6H_5N{=}S{=}O$ and $C_6H_{11}N{=}S{=}O$ at room temperature in a period of 7 h to several days, the complexes η^5-$C_5H_5Fe(CO)_2R$ ($R = CH_3$, $CH_2C_6H_5$) react readily with the more electrophilic *N*-sulfinylsulfonamides, $CH_3S(O)_2N{=}S{=}O$ and p-$CH_3C_6H_4S(O)_2N{=}S{=}O$. Typically, η^5-$C_5H_5Fe(CO)_2R$ and a slight excess of $R'S(O)_2N{=}S{=}O$ in toluene or $CHCl_3$ were allowed to react at room temperature for 1 h to yield a deep red solution. Excess $R'S(O)_2N{=}S{=}O$ was destroyed with 10% H_2O in acetone, solvent was removed, the residue was extracted with $CHCl_3$, and the extract was dried over $MgSO_4$ and filtered. Since the products resist crystallization, they were generally isolated by evaporation of the solvent to leave orange-red glasses. Elemental analysis shows them to be 1/1 adducts of the two reactants*, and their *N*-(alkylsulfinyl)alkanesulfonamidato-*N* structures (Ia—Id) are inferred from the spectroscopic data set out in Table 1. All complexes I exhibit three IR $\nu(SO_2)$ and $\nu(SO)$ absorptions at 1300, 1146—1135, and 1085—1080 cm^{-1}, which may be compared with those at 1350, 1165, and 1080 cm^{-1}, reported [1] for the organic cycloadducts of 1,3-dienes and $RS(O)_2N{=}S{=}O$ (A).



(A)

Complexes Ia—Ic undergo oxidation by *m*-$ClC_6H_4C(O)OOH$ to the corresponding *N*-(alkylsulfonyl)alkanesulfonamidato-*N* derivatives (IIa—IIc)**.

In a typical reaction, Ia—Ic in CH_2Cl_2 was treated with a slight excess of *m*-$ClC_6H_4C(O)OOH$, and the resulting solution was stirred for 1 h. Excess acid was neutralized with $NaHCO_3$ in methanol; then solvent removal, extraction of



(a: $R = R' = CH_3$; b: $R = CH_3$, $R' = p$-$CH_3C_6H_4$; c: $R = CH_2C_6H_5$, $R' = CH_3$; d: $R = CH_2C_6H_5$, $R' = p$-$CH_3C_6H_4$)

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*Ia: Found: C, 32.32; H, 3.23; S, 19.18. $C_9H_{11}FeNO_5S_2$ calcd.: C, 32.45; H, 3.33; S, 19.25%.
Ib: Found: C, 44.85; H, 4.18; S, 15.49. $C_{15}H_{15}FeNO_5S_2$ calcd.: C, 44.02; H, 3.69; S, 15.67%.

**IIa: Found: C, 30.85; H, 3.10; S, 18.12. $C_9H_{11}FeNO_6S_2$ calcd.: C, 30.96; H, 3.18; S, 18.36%.

TABLE 1

SPECTROSCOPIC DATA FOR NEW IRON COMPLEXES

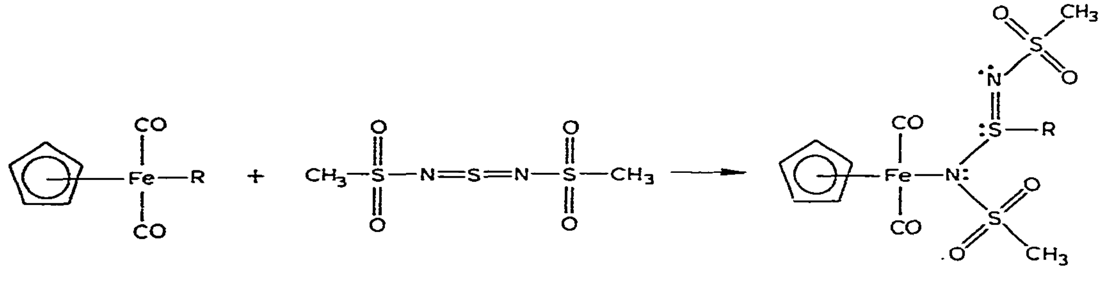
Complex	IR (cm^{-1})		^1H NMR (τ, ppm) [c]	^{13}C NMR (δ, ppm) [d]
	$\nu(CO)$ [a]	$\nu(SO_2)$, $\nu(SO)$, $\nu(SN)$ [b]		
Ia [e]	2050, 2000 [i]	1300, 1135, 1080	4.77(C_5H_5), 7.08(O_2SCH_3), 7.49($OSCH_3$)	212.2, 211.5(CO), 85.8(C_5H_5), 45.1(O_2SCH_3), 41.9($OSCH_3$)
Ib	2060, 2015	1300, 1145, 1080	4.72(C_5H_5), 7.42, 7.81(CH_3) [k]	
Ic	2055, 2010 [i]	1300, 1140, 1080	4.94(C_5H_5), 5.72, 6.14(CH_2) [l], 7.23(CH_3)	212.2, 211.8(CO), 86.0(C_5H_5), 65.1(CH_2), 43.1(CH_3)
IIa	2070, 2020 [i]	1321, 1315, 1295, 1135	4.84(C_5H_5), 6.93(2CH_3)	210.9(CO), 85.6(C_5H_5), 42.7(2CH_3)
IIb	2059, 2014	1320, 1150, 1140	5.08(C_5H_5), 6.90(SCH_3), 7.56 (CCH_3)	
IIc	2056, 2012	1325, 1298, 1130	5.29(C_5H_5), 5.36(CH_2), 6.95 (CH_3)	210.9(CO), 86.0(C_5H_5), 60.2(CH_2), 42.1(CH_3)
IIIa [f]			4.70(C_5H_5), 6.60($OSCH_3$), 7.00 (O_2SCH_3)	
IIIb	2070, 2022	1295, 1280, 1145, 1115, 1088, 1025, 1010	4.69(C_5H_5), 6.65(SCH_3), 7.63 (CCH_3)	208.8, 208.0(CO), 87.9(C_5H_5), 59.4(SCH_3), 21.4(CCH_3)
IIIc	2065, 2005 [j]	1275, 1130, 1105, 1030	4.92(C_5H_5), 5.33(CH_2), 6.99 (CH_3)	(CO) [n], 87.6(C_5H_5), 75.9(CH_2), 45.6(CH_3)
[g]			4.75(C_5H_5), 6.85(CH_3) [9]	210.1(CO), 87.6(C_5H_5), 60.6(CH_3)
[h]			4.90(C_5H_5), 5.61(CH_2) [9]	209.7(CO), 87.2(C_5H_5), 78.0(CH_2)
IVa	2042, 2003, 1989 [j]	1300, 1280, 1128, 1012	4.70(C_5H_5), 6.91, 7.04, 7.39 (CH_3)	(CO) [n], 85.8(C_5H_5), 43.2, 42.4 (O_2SCH_3), 39.1(N_2SCH_3)
IVb	2050, 2005 [j]	1310, 1295, 1288, 1150, 1140, 1020, 1010	4.73(C_5H_5), 5.79, 5.91(CH_2) [m], 6.90(SCH_3), 7.64(CCH_3)	212.0, 210.7(CO), 85.8(C_5H_5), 59.9(CH_2), 42.8, 42.0(CH_3)

[a] In $CHCl_3$ solution except as noted. All absorptions are strong. [b] In Nujol mull. Only strong absorptions are listed. [c] In $CDCl_3$ solution except as noted. Only resonances of the C_5H_5, CH_2, and CH_3 groups are listed. [d] In $CDCl_3$ solution, ppm downfield from $Si(CH_3)_4$. Only resonances of the CO, C_5H_5, CH_2, and CH_3 groups are listed. [e] Parent peak at m/e 333 in the mass spectrum. [f] Complex not isolated pure. [g] η^5-$C_5H_5Fe(CO)_2S(O)_2CH_3$. [h] η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2C_6H_5$. [i] In CH_2Cl_2 solution. [j] In Nujol mull. [k] In C_6F_6 solution. In $CDCl_3$ solution: 4.83(C_5H_5), 7.60(2CH_3). [l] J_{AB} 12.4 Hz. [m] J_{AB} 12.1 Hz. [n] Signal too weak for accurate measurement.

the residue with CH_2Cl_2, and evaporation to dryness of the extract yielded a red solid, which may be recrystallized from 1/1 CH_2Cl_2/hexane at low temperature. The synthesis of IIa from Ia in this manner is particularly illuminating with respect to the assignment of structure. The two CH_3 signals in each of the ^1H and ^{13}C NMR spectra of Ia (Table 1) collapse to a single resonance upon oxidation of Ia to IIa. The equivalence of the CH_3 groups in IIa is consistent only with the proposed symmetrical *N*-(methylsulfonyl)methanesulfonamidato-*N* structure. Moreover, these data also corroborate the *N*-(methylsulfinyl)methanesulfonamidato-*N* structural assignment to the precursor Ia.

Storage of Ia—Ic in the solid or in solution leads to the formation of yellow-orange solids which appear to be the rearranged *N*-(alkylsulfonyl)alkanesulfinimidato-*S* complexes (IIIa—IIIc). For example, IIIc was isolated by slow (several days) crystallization from saturated $CHCl_3$ solution of Ia at –10°C. Support for the proposed structure is derived from the spectroscopic data included in Table 1. Thus, the ^1H NMR signals of the CH_3 and CH_2 groups bound to the sulfinyl sulfur experience a considerable (0.60—0.95 ppm) downfield shift from the corresponding signals of Ia—Ic. A similar deshielding of the O_2SCH_3 and O_2SCH_2 protons has been noted upon isomerization of *O*-bonded to *S*-bonded sulfinato complexes [8]. In the ^{13}C NMR spectra, the resonances of each of the carbonyl (210.1—208.0), C_2H_5 (87.9—87.2), and, especially, CH_2 (78.0—75.9) and CH_3 (60.6—59.4 ppm) groups bound to sulfur, occur in distinct narrow ranges for both III and similar, previously reported [9], *S*-sulfinato complexes. However, these ranges are different from those for the corresponding resonances of complexes I, II, and IV (CO, 212.2—210.7; C_5H_5, 86.0—85.6; SCH_2, 65.1—59.9; SCH_3 45.6—39.1 ppm).

The reaction of η^5-$C_5H_5Fe(CO)_2R$ ($R = CH_3$, $CH_2C_6H_5$) with excess $CH_3S(O)_2$-$N{=}S{=}NS(O)_2CH_3$ in $CHCl_3$ leads to the formation of a deep red solution. Unreacted, sparingly soluble sulfur diimide was filtered off and the product formulated as IVa—IVb* was crystallized at low temperature from $CHCl_3$.



(IVa-IVb)

(a: R = CH_3 ; b: R = $CH_2C_6H_5$)

Spectroscopic data of IVa—IVb are incorporated into Table 1. In the IR 1350—950 cm^{-1} region strong stretching absorptions of the SO_2 and SN groups occur which are similar to those at 1370—1345, 1180—1160 ($\nu(SO)_2$) of NSO_2), 1310—1280, 1160—1120 ($\nu(SO_2)$ of $=NSO_2$), and 1010—975 cm^{-1} (ν(SN)) re-

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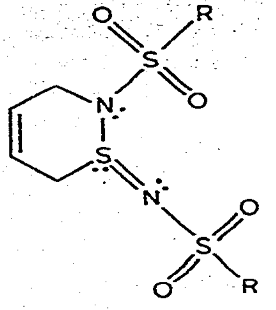
*IVb: Found: C, 39.55; H, 3.86; S, 18.92. $C_{16}H_{18}FeN_2O_6S_3$ calcd.: C, 39.51; H, 3.73; S, 19.78%.

ported [10] for the organic cycloadducts of 1,3-butadiene and $RS(O)_2N{=}S{=}NS(O)_2R$ (B). Each of the ^1H and ^{13}C NMR spectra of IVa shows three CH_3 signals, consistent with the proposed *N*-[*S*-methyl-*N'*-(methylsulfonyl)sulfinimidoyl]-methanesulfonamidato-*N* structure. The complexes do not exhibit fluxional behavior at ambient temperatures.



(B)

The foregoing reactions demonstrate that $RS(O)_2N{=}S{=}O$ and $CH_3S(O)_2N{=}S{=}NS(O)_2CH_3$, like SO_2 itself, readily undergo insertion into the Fe—R bonds of η^5-$C_5H_5Fe(CO)_2R$. As with SO_2, the initial products contain the harder, in this case nitrogen, donor atom bonded to the metal. It remains to be elucidated whether all three reactions are similar mechanistically; studies of the stereochemistry at α-carbon of the insertion of $RS(O)_2N{=}S{=}O$ and $RS(O)_2N{=}S{=}NS(O)_2R$ are in progress toward this end.

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References

1 G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H.P. Patzschke, H. Smalla and A. Trede, Angew. Chem. Int. Ed., 1 (1962) 89.
2 G. Kresze and W. Wucherpfennig, Angew. Chem. Int. Ed., 6 (1967) 149.
3 H.J. Backer and J. Strating, Rec. Trav. Chim. Pays-Bas, 62 (1943) 815.
4 D.M. Blake and J.R. Reynolds, J. Organometal. Chem., 113 (1976) 391 and cited ref.
5 R. Meij, T.A.M. Kaandorp, D.J. Stufkens and K. Vrieze, J. Organometal. Chem., 128 (1977) 203 and cited ref.
6 R.R. Ryan and P.G. Eller, Inorg. Chem., 15 (1976) 494.
7 A. Wojcicki, Advan. Organometal. Chem., 12 (1974) 31.
8 S.E. Jacobson, P. Reich-Rohrwig and A. Wojcicki, Inorg. Chem., 12 (1973) 717.
9 J.P. Bibler and A. Wojcicki, J. Amer. Chem. Soc., 88 (1966) 4862.
10 W. Wucherpfennig and G. Kresze, Tetrahedron Letters, 15 (1966) 1671.