

- preliminary pyrolysis experiments.
- (8) The compound was sublimed with gentle heat into a quartz tube packed with quartz beads, and pyrolysis products were collected on a cold finger ( $-78^{\circ}\text{C}$ )  $\sim 1$  cm from the hot zone; chloroform was then distilled from another vessel to wash the product from the cold finger into a collection tube.
  - (9) Chromatography on silica gel or basic alumina destroyed the product. It could be purified on Florisil (hexane eluant), but some decomposition occurred if contact with Florisil was prolonged.
  - (10) At 60 MHz, only a sharp singlet at  $\delta$  3.25 is seen.
  - (11) The limited solubility and the long relaxation time of the ring carbons caused the lowest field peak to be weak and difficult to observe.
  - (12) For example, the methylene protons of naphtho[a]cyclobutene and naphtho[b]cyclobutene appear at  $\delta$  3.25 and  $\delta$  3.28, respectively (R. P. Thummel, W. E. Cravey, and W. Nutakul, *J. Org. Chem.*, **43**, 2473 (1978)), and those of acenaphthene and several pyracene derivatives occur in the range of  $\delta$  3.37–3.49 (L. A. Carpino and S. Gowecke, *J. Org. Chem.*, **29**, 2824 (1964) and B. M. Trost, G. M. Bright, C. Frihart and C. Brittelli, *J. Am. Chem. Soc.*, **93**, 737 (1971)). The methylene carbons appear at  $\delta$  28.27 and 29.26 in naphtho[a]cyclobutene (we are indebted to Professor Thummel for sending us various spectra for comparison) and at  $\delta$  31.5 in pyracene (B. M. Trost and W. B. Herdle, *J. Am. Chem. Soc.*, **98**, 4080 (1976)). Although these data tend to favor **6** over **7**, it is difficult to predict how the combined presence of four- and five-membered rings in **7** will affect the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts.
  - (13) Other spectral data of the product follow: IR (KBr) 2900–2920 (s), 2820 (s), 1600 (m), 1478 (w), 1440 (w), 1416 (m), 1365 (s), 1272 (m), 1212 (m), 1192 (m), 1154 (w), 815 (w), 760 (w),  $713\text{ cm}^{-1}$  (w); UV (5:2 methylene chloride–acetonitrile)  $\lambda_{\text{max}}$  360 nm ( $\epsilon$  310), 335 (620), 309 (4790), 298 (6040), 286 (4630), 270 (sh), 240 (47 500); a methylene chloride solution irradiated at 298 nm showed fluorescence with a maximum at 355–360 nm. The ultraviolet spectrum shows some similarity to that of pyracene (A. G. Anderson, Jr., and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952)).
  - (14)  $R = 4.6\%$ ,  $R_w = 3.5\%$ , estimated standard deviation 0.004–0.008 Å and 0.3–0.6°. Details of the structure will be reported in *Acta Crystallogr.*
  - (15) The quartz beads, following the pyrolysis of either **4** or **5**, were coated with a hard, steely-gray bright mirror which was extremely difficult to remove mechanically, but which could be removed by combustion. This type of mirror was not produced during the pyrolysis of **8**, suggesting that it may be a polymer of **3**, reminiscent of the films produced from *p*-xylylene vapors (L. A. Errede and M. Szwarc, *Q. Rev., Chem. Soc.*, **12**, 301 (1959)).
  - (16) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4269 (1972).

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Avraham Teuerstein, Donald L. Ward

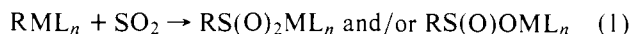
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Received July 25, 1978

### A Radical-Chain Mechanism for Some Sulfur Dioxide "Insertion" Reactions in Organocobaloximes

Sir:

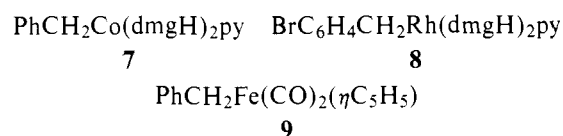
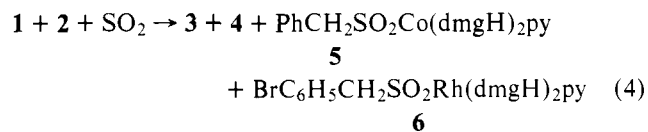
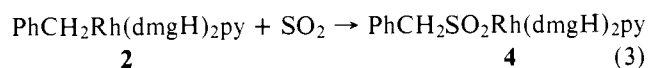
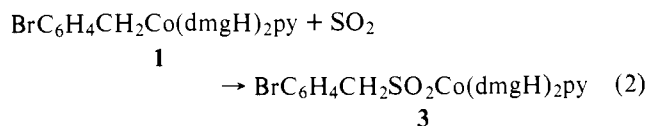
Sulfur dioxide insertion is one of the more common reactions of  $\sigma$ -bonded organometallic complexes;<sup>1</sup> it occurs with many organic derivatives of both main group and transition elements (eq 1). However, despite the appreciable body of careful work on the kinetics, products, and stereochemistry of these reactions, there is no comprehensive picture of the mechanisms which may operate.



We here describe some simple experiments which demonstrate that, in the case of certain organocobaloximes,<sup>2</sup> organorhodoximes, and possibly in the case of some organoiron complexes under appropriate conditions, the reaction is not a true insertion into the carbon–metal bond, but is an intermolecular process in which the organic and metal fragments of the "insertion" product do not originate from the same molecule of organometallic substrate.

Thus, 4-bromobenzylbis(dimethylglyoximate)pyridinecobalt(III) (**1**) and benzylbis(dimethylglyoximate)pyridinerhodium(III) (**2**) separately undergo "insertion" in liquid  $\text{SO}_2$  in sealed tubes at ambient temperature within 2 h to give the corresponding products **3** and **4**, respectively<sup>2</sup> (eq 2, 3). Under identical conditions, an equimolar mixture of **1** and **2** reacts to give four products, **3**, **4**, **5**, and **6**<sup>3</sup> (eq 4). In the early stages product **4** is formed faster than **5** and **6**, and **3** is formed slowest

of all. No rearrangement of **1** and **2** into **7** and **8** takes place during the reaction,<sup>4</sup> and separate experiments in which reaction **3** is carried out in the presence of the insertion product **3** show that no conversion of **3** and **4** into **5** and **6** occurs.<sup>5</sup>

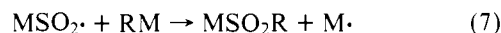
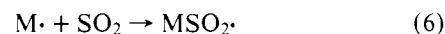


Following our several recent observations of chain reactions involving homolytic displacements at carbon centers,<sup>6</sup> we propose that these apparent sulfur dioxide insertion reactions involve the radical-chain mechanism outlined below.

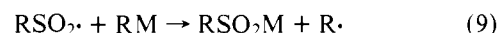
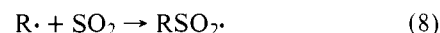
Initiation:<sup>7</sup>



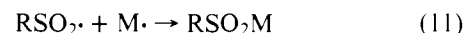
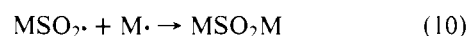
Propagation:



and/or

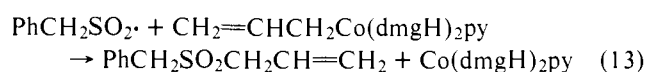
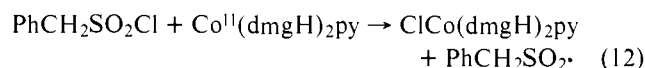


Termination:

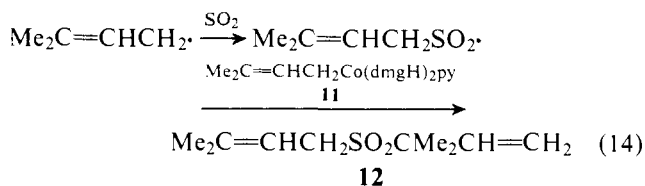


The radical nature of the reaction is apparent from observations that (i) the reactions of  $\text{SO}_2$  with alkylcobaloximes at low temperatures, e.g., with  $\text{PhCH}_2\text{CH}_2\text{Co}(\text{dmgH})_2\text{py}$ , are markedly photocatalyzed<sup>8</sup> and (ii) the rates of thermal reaction of  $\text{SO}_2$  with alkylcobaloximes are variable and subject to induction periods and to catalysis by admixture with the more reactive benzyl- or allylcobaloximes or with cobaloxime(II). While we cannot rule out some reaction through the propagation steps **8** and **9**, we prefer the mechanism involving predominantly reactions **5**, **6**, **7**, and **10** for the following reasons.

(a)  $\alpha$ -Toluenesulfonyl radicals, generated by chlorine atom abstraction from the corresponding  $\alpha$ -toluenesulfonyl chloride by cobaloxime(II) (eq 12), react with allylcobaloximes to give high yields of the benzyl(allyl)sulfone (**10**, eq 13), but no "insertion" product **5** can be detected.<sup>9</sup> Moreover, only small yields of **5** are formed in the reaction of  $\alpha$ -toluenesulfonyl chloride with **7** despite significant formation of chlorocobaloxime(III) via eq 12.

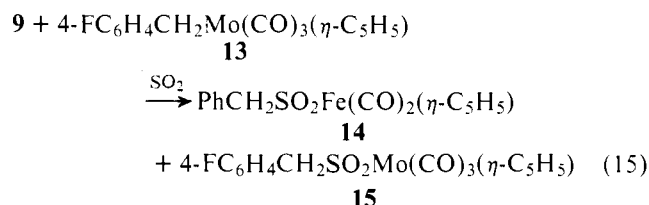


Clearly, reaction 9, which is a key step in the other possible chain mechanism (eq 8 and 9), is not a favorable process in the case of six-coordinate organocobaloximes; indeed, any organosulfonyl radicals which are formed during the reaction with sulfur dioxide may, in appropriate cases, undergo reaction with the organocobaloxime via a reaction analogous to eq 13 which regenerates cobaloxime(II) and thereby initiates reaction 6 of the preferred chain mechanism. It is not surprising therefore that some ( $\leq 5\%$ ) of the specific sulfone **12**<sup>10</sup> accompanies the insertion product in the reaction of dimethylallylcobaloxime (**11**) with SO<sub>2</sub> (eq 14).

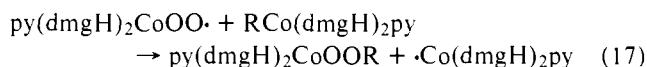
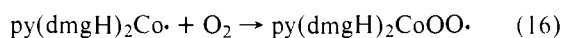


(b) There is good precedent for reaction 6 from the direct reactions of SO<sub>2</sub> with cobalt(II) complexes such as Co(CN)<sub>5</sub><sup>3-</sup> and Co(dmgH)<sub>2</sub>py. The former gives the well-characterized complex<sup>11</sup>  $\{[(\text{NC})_5\text{Co}]_2\text{SO}_2\}^{6-}$  supposedly via reactions 6 and 10, though the corresponding complex (py(dmgH)<sub>2</sub>Co)<sub>2</sub>SO<sub>2</sub> is less well characterized.<sup>12</sup> It is significant that the latter complex is also formed as a byproduct ( $\leq 10\%$ ) in the reaction of SO<sub>2</sub> with **1** and with **7**.<sup>13</sup>

The above mechanism is by no means universal in SO<sub>2</sub> insertion reactions, but may also apply to some organoiron complexes under extreme conditions. For example, though the insertion product **5** is also obtained in 5–15% yield<sup>14</sup> from the reaction of SO<sub>2</sub> with mixtures of either **9** with **1**, or **9** with CH<sub>3</sub>Co(dmgH)<sub>2</sub>py,<sup>15</sup> only the two normal insertion products **14** and **15** were formed in the reaction of SO<sub>2</sub> with a mixture of **9** and **13**<sup>16</sup> (eq 15).



The implications of the above results are twofold. First, though the free-radical-chain mechanism is dominant in the case of some organocobaloximes and organorhodoximes, it may intrude in other systems only where there is sufficient initiation and where the concentrations are sufficiently high and the stability of the displaced metal such that the propagation step 7 is favored. Second, the sulfur dioxide insertion reactions of organocobaloximes show remarkable similarities of initiation, rates, and regioselectivity to the oxygen insertion reactions of the same complexes.<sup>18</sup> We have endeavored to investigate the intermolecular character of the oxygen insertion in the same manner as above, but have been thwarted by the ready exchange of organic groups between substrates<sup>19</sup> prior to the reaction with oxygen and catalyzed by traces of cobaloxime(II) in solution. However, the analogies are so close for us to propose that some oxygen insertion reactions of the cobaloximes also involve radical-chain reactions, with the same initiation step as for sulfur dioxide insertion, and the corresponding propagation steps of eq 16 and 17.



**Acknowledgments.** We thank Dr. Alain Gaudemer for many

interesting discussions which have played a substantial part in formulating the experimental work and the conclusions described, the Science Research Council for financial support (to A.E.C.), and NATO for a travel award for discussions with Dr. J. H. Espenson (to M.D.J.).

## References and Notes

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- (2) M. D. Johnson and G. J. Lewis, *J. Chem. Soc. A*, 2153 (1970); C. J. Cooksey, D. Dodd, C. Gatford, M. D. Johnson, G. J. Lewis, and D. M. Titchmarsh, *J. Chem. Soc., Perkin Trans. 2*, 655 (1972), describe the insertion reactions of organocobaloximes, but insertion into organorhodoximes has not been described.
- (3) The benzylrhodoxime **2** is slightly more reactive and hence the appearance of **5** and **6** in preference to **3** indicates that the rhodoxime(II) species is more readily displaced by MSO<sub>2</sub>· when M = Co(dmgH)<sub>2</sub>py or Rh(dmgH)<sub>2</sub>py. A necessary consequence is that the yields of **5** and **6** should be the same, which is what is observed.
- (4) The several reagents and insertion products were detected in the reaction mixtures by <sup>1</sup>H NMR and confirmed by isolation after TLC. Only pairs of compounds, e.g., **3** and **5**, could be obtained, but these could be prepared separately by other methods and positively identified in and from the reaction mixtures.
- (5) Reaction 2 was allowed to proceed to completion and mixed with the reagents of reaction 3. After 2 h, reaction 3 was complete and only two insertion products, **3** and **4**, were present.
- (6) (a) T. Funabiki, B. D. Gupta, and M. D. Johnson, *J. Am. Chem. Soc.*, **98**, 6697 (1976); (b) *J. Chem. Soc., Chem. Commun.*, 653 (1977); (c) K. N. V. Duong, A. Gaudemer, and M. D. Johnson, unpublished work; (d) C. J. Cooksey, D. Dodd, M. D. Johnson, and B. L. Lockman, *J. Chem. Soc., Dalton Trans.*, in press; (e) A. Bury, C. J. Cooksey, T. Funabiki, B. D. Gupta, and M. D. Johnson, *J. Chem. Soc., Perkin Trans. 2*, in press; (f) A. E. Crease, B. D. Gupta, and M. D. Johnson, *J. Chem. Soc., Dalton Trans.*, in press.
- (7) Since most organocobaloximes contain traces of cobaloxime(II) species, particularly in solution in the light, there is usually no need for an induced initiation step.
- (8) Tungsten lamps (2 × 150–500 W at 10 cm) using water-cooled all-glass apparatus.
- (9) A. E. Crease and M. D. Johnson, unpublished observations.
- (10) Some O-(2-methylbut-3-en-2-yl)dimethylglyoxime ( $\leq 10\%$ ) is also formed.
- (11) A. A. Vlcek and F. Basolo, *Inorg. Chem.*, **5**, 156 (1966).
- (12) M. D. Johnson and G. J. Lewis, unpublished observations.
- (13) During many of the reactions of organocobaloximes with sulfur dioxide, the <sup>1</sup>H NMR spectra quickly become broad owing to the presence of paramagnetic cobaloxime(II) species, but sharpen again toward the end of each reaction. The lack of reaction of methyl(pyridine)cobaloxime with pure dry sulfur dioxide reported earlier<sup>2</sup> may have been a result of the absence of radical initiation rather than, as proposed earlier, the absence of water.
- (14) Implying attack of py(dmgH)<sub>2</sub>CoSO<sub>2</sub>· radicals on the organoiron complex, but not necessarily attack of (η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>FeSO<sub>2</sub>· radicals on the organocobaloxime.
- (15) These substrates do not insert at the same rates and hence the extent of formation of crossed products would not be expected to be large.
- (16) These substrates react with SO<sub>2</sub> at almost identical rates and hence would be expected to give near-statistical yields of crossed and uncrossed products in an intermolecular radical mechanism. Jacobsen and Wojcicki<sup>17</sup> have demonstrated a similar lack of crossed products in the reactions of SO<sub>2</sub> with mixtures of **9** and other organomolybdenum complexes.
- (17) S. E. Jacobsen and A. Wojcicki, *J. Am. Chem. Soc.*, **95**, 6962 (1973).
- (18) C. Bied-Charreton and A. Gaudemer, *J. Organomet. Chem.*, **124**, 299 (1977), and references quoted therein.
- (19) D. Dodd, M. D. Johnson, and B. L. Lockman, *J. Am. Chem. Soc.*, **99**, 3664 (1977).

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Received March 14, 1978

## Inhibition of 5-Phosphomevalonate Kinase by an Isosteric Analogue of 5-Phosphomevalonate

Sir:

Analogues of the prenyl diphosphate intermediates of sterol biosynthesis proved to be useful probes for testing some enzymic functions<sup>1</sup> and specificities<sup>2</sup> and may point to the design of new substances inhibiting cholesterol biosynthesis.<sup>3</sup> The usefulness of the diphosphate analogues of, e.g., geranyl diphosphate, such as citronellyl, tetrahydrogeranyl, or octyl di-