

Organocobaloximes in organic synthesis An unusual radical-dependent five-member cyclization

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Abstract

Visible light photolysis of organocobaloximes $R'C\equiv C(CH_2)_3-Co^{III}(dmgH)_2Py$ **1–3** ($R' = Ph, TMS, H$) with radical trapping agents $ArSO_2Cl$ ($Ar = Ph, 4-MeC_6H_4, 4-OMeC_6H_4, 4-BrC_6H_4, 4-ClC_6H_4$) and $MeSO_2Cl$ afford rearranged or non-rearranged organic products depending on the R' group. 2-Phenylcyclopentenyl sulfones **4a–4f** have been obtained exclusively in the case of cobaloxime **1**.
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1. Introduction

Metal-mediated intramolecular radical cyclization involving an acetylenic appendage has matured into an area of gainful importance leading to the synthesis of complex carbocycle frameworks [1]. While a synthetic organic chemist would prefer to generate the radical of choice in situ starting from an all-organic precursor, an organometallic chemist relies on a preformed organometallic reagent to begin with. The latter approach continues to provide useful information on the mechanism of cyclization and stereoelectronic demand of the transition state.

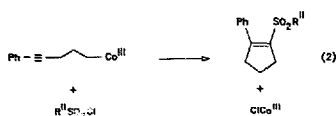
We have long been interested in the free radical chemistry of organobis(dimethylglyoximate)(pyridine)cobalt(III) complexes, trivially known as organocobaloximes [2,3]. Owing to the very low metal–carbon bond energy ($17–26 \text{ kcal mol}^{-1}$) in the complexes, uni-

molecular homolysis of $R-Co(III)$ can be readily effected by irradiation with visible light which reversibly generates $R^\cdot$ and $Co(II)$ (Scheme 1) [4]. If favourably poised, $R^\cdot$ may cyclize to $R'^\cdot$ and upon recapture by $Co(II)$ would afford isomeric cobaloxime $R'-Co(III)$ [5]. In the presence of an organic radical trap $Y^\cdot$ (even a solvent as hydrogen or halogen trap) exclusive or partial formation of RY or $R^\cdot Y$ takes place depending on the relative rates k_1 , k_2 and k_c .

We have recently disclosed the efficient trapping of 5-phenylpent-4-ynyl radical in the reaction of 5-phenylpent-4-ynyl cobaloxime **1** with various heteroatom radicals which cleanly afford the corresponding non-rearranged organic products (Eq. 1) [2]. While extending the reaction to organosulfonyl radicals we have noticed a novel five member cyclization leading to the corresponding cyclopentenyl sulfones **4** (Eq. 2). We wish to present these observations in this report.



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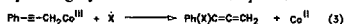


2. Results

All the reactions were generally performed with cobaloxime (1 mM) and organosulfonyl chlorides (1.5 mM) in dry methylene chloride (30 ml) at -2 to 0°C under irradiation with a 500 W sunlamp in inert nitrogen atmosphere followed by product isolation by flash chromatography. The reaction of 5-phenylpent-4-ynyl cobaloxime **1** with 4-methylbenzenesulfonyl chloride affords 2-phenyl-cyclopentenyl(tolyl)sulfone **4a** as the only organic product in 72% isolated yield, the inorganic product being chlorocobaloxime **5** (Table 1, entry 1). Similar reactions of **1** with various arenesulfonyl chlorides gave exclusively the corresponding cyclized sulfones **4b–4e** in 70–87% yields (entries 2–5). Methanesulfonyl chloride, however, gives a mixture of 2-phenylcyclopentenyl(methyl)sulfone **4f** and 5-phenylpent-4-ynyl chloride **4g** in 50% and 26% yields respectively. Here, methanesulfonyl cobaloxime **6** is formed as the second inorganic product besides chlorocobaloxime **5**. Attempts to extend the above reaction with 5-trimethylsilylpent-4-ynyl cobaloxime **2** and pent-4-ynyl cobaloxime **3** led to unexpected formation of pent-4-ynyl halides **2a** and **3a** respectively as the sole organic products; the corresponding organosulfonyl cobaloximes being **6**, **7** and **8** (Table 2). All the compounds were fully characterized by spectral and analytical data. Furthermore, the structure of **4f** has been confirmed by X-ray crystal structure determination. An ORTEP plot is presented (Fig. 1) along with bond lengths (Table 3) and bond angles data (Table 4).

The results assume further interesting contrast when compared with homologous alkynyl cobaloximes of varying chain length [5]. Thus, in 3-phenylprop-2-ynyl cobaloxime, radical attack takes place exclusively at the terminal acetylenic centre, that is at the gamma carbon

(Eq. 3), whereas 6-phenylhex-5-ynyl cobaloxime and 7-phenylhept-6-ynyl cobaloximes, upon irradiation by visible light, undergo facile rearrangement to the corresponding cyclic cobaloximes (Eq. (4)).



The following independent observations relevant to determination of the mechanism of the reactions were made.

(1) In the absence of added reagent no rearrangement or decomposition of cobaloximes **1–3** takes place upon extended photolysis, after which they are recovered back quantitatively.

(2) The reactions mentioned above show a distinct concentration-dependent induction period which could be monitored by TLC and unequivocally by NMR. Thus, when **1** and 4-methylbenzenesulfonyl chloride in CDCl_3 are reacted in a sealed NMR tube under the above photolysis condition, but at 10°C , and the methyl signal of the reacting halide is monitored, an unambiguous induction period of 1.5 h could be observed (Fig. 2). This induction period could be considerably reduced by the addition of 0.01 mole equivalents of cobaloxime(**1**), while 0.01 mole equivalents of galvinoxyl, a well-known radical trap, inhibited the reaction so that the induction period was increased to 6 h.

(3) The reaction showed no free radical chain behaviour. Thus, after the induction period the reaction stops as the light source is turned off; it restarts after a

Table 1
Formation of 2-phenylcyclopentenyl sulfones (**4a–4f**) from $\text{PhC}\equiv\text{CCH}_2\text{CH}_2\text{M}^{\text{II}}$ and organosulfonyl chlorides ($\text{R}^{\text{II}}\text{SO}_2\text{Cl}$)^a

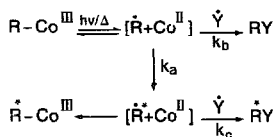
Entry	R ^{II}	Time (h)	Sulfone	Yield ^c (%)
1	4-MeC ₆ H ₄	15	4a	72
2	4-OMeC ₆ H ₄	20	4b	75
3	4-BrC ₆ H ₄	16	4c	87
4	4-ClC ₆ H ₄	14	4d	70
5	Ph	18	4e	78
6	Me	24	4f ^d	50

^a M = Co^{III}(dmgH), Py.

^b Inorganic product ClM^{II} unless otherwise stated.

^c Refers to isolated yield with respect to **1**.

^d Along with 5-phenylpent-4-ynyl chloride **4g** (26%), inorganic product **5** + MeSO₂M **6**.



Scheme 1.

Table 2

Products from reactions of $R'C\equiv CCH_2CH_2CH_2M$ (2 and 3) with organosulfonyl chlorides ($R''SO_2Cl$)

Entry	R'	R''	Time (h)	Organic product	Yield ^a (%)	Inorganic product ^b
1	TMS 2	4-MeC ₆ H ₄	16	TMSC=C(CH ₂) ₃ Cl 2a	47	TsM 7 ^c
2		4-BrC ₆ H ₄	15	2a	49	BrSM 8 ^c
3		Me	20	2a	45	MsM 6 ^c
4	H 3	4-MeC ₆ H ₄	14	HC≡C(CH ₂) ₃ Cl 3a	45 ^d	TsM 7
5		4-BrC ₆ H ₄	14	3a	45 ^d	BrSM 8
6		Me	15	3a	50 ^d	MsM 6

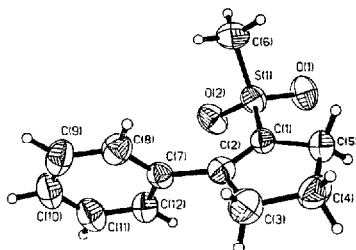
^a Refers to isolated yield with respect to starting cobaloxime, unless otherwise stated.^b Ts = 4-methylbenzenesulfonyl; Brs = 4-bromobenzenesulfonyl; Ms = methanesulfonyl.^c Additional inorganic product is 5.^d NMR yield along with uncharacterized organic products.

Fig. 1. Perspective view of compound 4f showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels, except for H atoms which are drawn as small circles of arbitrary radius.

further period of induction when the light source is again turned on. It should be noted that the individual times shown in Tables 1 and 2 are for reactions under constant illumination and do not include the induction period.

(4) When the reactions are carried out in the presence of oxygen there is a sharp decrease in the product yields and many ill-defined products are obtained.

Table 3

Bond lengths (Å)

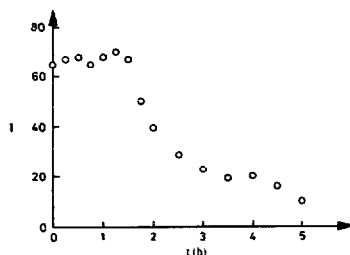
S(1)–O(1)	1.447(3)
S(1)–O(2)	1.441(3)
S(1)–C(1)	1.766(4)
S(1)–C(6)	1.758(4)
C(1)–C(2)	1.338(5)
C(1)–C(5)	1.513(6)
C(2)–C(3)	1.515(5)
C(2)–C(7)	1.493(5)
C(3)–C(4)	1.544(6)
C(4)–C(5)	1.518(6)
C(7)–C(8)	1.391(6)
C(7)–C(12)	1.389(5)
C(8)–C(9)	1.390(6)
C(9)–C(10)	1.371(7)
C(10)–C(11)	1.377(7)
C(11)–C(12)	1.393(6)

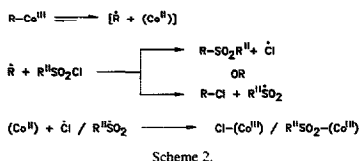
Table 4

Bond angles (deg)

O(1)–S(1)–O(2)	118.2(2)
O(1)–S(1)–C(1)	107.0(2)
O(2)–S(1)–C(1)	110.2(2)
O(1)–S(1)–C(6)	108.3(2)
O(2)–S(1)–C(6)	107.9(2)
C(1)–S(1)–C(6)	104.5(2)
S(1)–C(1)–C(2)	126.1(3)
S(1)–C(1)–C(5)	120.0(3)
C(2)–C(1)–C(5)	113.7(3)
C(1)–C(2)–C(3)	110.1(3)
C(1)–C(2)–C(7)	132.1(3)
C(3)–C(2)–C(7)	117.8(3)
C(2)–C(3)–C(4)	104.8(3)
C(3)–C(4)–C(5)	107.5(3)
C(1)–C(5)–C(4)	103.6(3)
C(2)–C(7)–C(8)	119.5(3)
C(2)–C(7)–C(12)	121.2(3)
C(8)–C(7)–C(12)	119.2(4)
C(7)–C(8)–C(9)	120.4(4)
C(8)–C(9)–C(10)	119.5(4)
C(9)–C(10)–C(11)	121.1(4)
C(10)–C(11)–C(12)	119.5(4)
C(7)–C(12)–C(11)	120.2(4)

(5) Reactions carried out under thermal conditions in refluxing methylene chloride or benzene give the same products, but, compared with the photochemical reactions, there are marked differences in the induction

Fig. 2. ¹H NMR decay profile for the reaction of 1 with TsCl. $I = [I(Me)/I(CH_2Cl_2)] \times 100$.



period, the subsequent reaction time and, in a few cases, the yield of the products. Attempted reaction in acetonitrile as solvent met with a complicated product mixture.

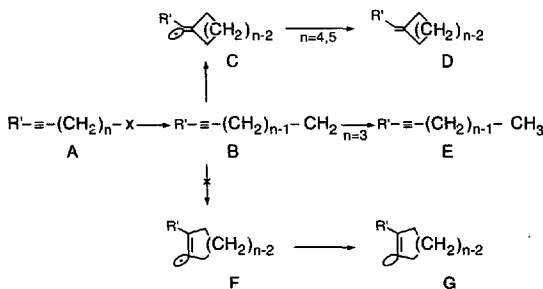
The results presented above point clearly to a non-chain free radical route for the reactions of cobaloximes **1–3** with the sulfonyl radical precursor $\text{R}^{\text{II}}\text{SO}_2\text{Cl}$. The features of this mechanism (Scheme 2) are (i) homolysis of R-Co^{III} (where $\text{R} = \text{R}'\text{-C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2$ and $\text{R}' = \text{Ph, TMS, H}$) to give an inert radical pair containing R' and (Co^{II}) ; (ii) atom(group) transfer from $\text{R}^{\text{II}}\text{SO}_2\text{Cl}$ by R' in a bimolecular process and (iii) coupling of (Co^{II}) with the counter radical (Cl or $\text{R}^{\text{II}}\text{SO}_2$) formed in step (ii). The fact that the dimerized product resulting from R' could not be detected, even in trace amounts, in any of the reactions, leads us to conclude that, at any given time, the concentration of free R' in solution is extremely low. The influence of galvinoxyl, a well-known radical scavenger, in delaying the induction period is also consistent with the proposed mechanism. Thus, as long as it is present in solution, galvinoxyl will efficiently quench any R' generated by the homolysis of R-Co^{III} , thereby totally inhibiting the radical trapping reaction. The formation of ill-defined products in reactions conducted in the presence of oxygen is not surprising. It is generally known that organocobaloximes undergo oxygen insertion under photostimulation to give $\text{ROO}(\text{Co}^{\text{II}})$, and the latter could react with the sulfonyl radical in many ways [6].

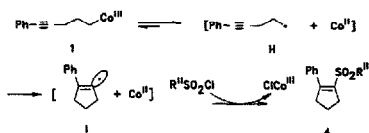
3. Discussion

The propensity of acetylenically radical cyclization, vis-à-vis carbometallation of the initial organometallic precursor, has been the subject of several investigations [1,7–14]. Pioneering work by Crandall and coworkers has confirmed the influence of alkyl chain length n and substituent R' on the acetylenic appendage in directing the cyclization (Scheme 3, A, X = Cl, Br, I). Favourable exo-dig cyclization is only obtained when $\text{R}' = \text{Ph}$ and $n = 4, 5$ (pathway $\text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow \text{D}$) [7–10]. The stabilization of the vinyl radical transition state **C** could be attributed to the conjugative influence of the aromatic appendage. Attempts to cyclize the lower homologue radical (**B**, $n = 3$, $\text{R}' = \text{Ph}$) via Zn [7], $\text{Cr}(\text{II})$ [8] or Bu_3SnH [9] reduction of the corresponding halide met with failure, the non-rearranged hydrocarbon **E** being the only product. On the contrary Li -biphenyl reduction (a radical anion system) of **A** ($n = 3$, $\text{R}' = \text{Ph}$, $\text{X} = \text{Br}$) promotes cyclization, albeit in poor yield [9]. The related organometallic reagent **A** ($n = 3$, $\text{R}' = \text{Ph}$, $\text{X} = \text{Cp}_2\text{TiCl}$) undergoes facile carbometallation in the presence of Et_3AlCl_2 as Lewis acid; extrusion of the organometallic fragment by acid work-up finally gives the benzyldienecyclobutane derivative **D** in 42% overall yield [15]. In all of the examples above the cyclization mode is uniformly exo-specific, i.e. bond formation occurs at the acetylenic carbon nearest to the radical. To the best of our knowledge the corresponding endo-dig cyclization (pathway $\text{B} \rightarrow \text{F} \rightarrow \text{G}$) has not been reported so far.

The chemistry observed in the reactions of cobaloximes **1–3** augments various features of acetylenically radical discussed above, and is highlighted below.

(1) Inability of cobaloximes **1–3** to rearrange on photostimulation, even in very dilute solution (0.003 M l^{-1}), indicates the formation of a tight radical





Scheme 4.

pair between the alkyl radical and Co(II). This also excludes any carbometallation pathway during trapping experiments.

(2) Exclusive formation of non-rearranged products during trapping experiments with cobaloximes 2 and 3 is consistent with the earlier observation that cyclization is disfavoured for radicals bearing an alkyl substituent on the acetylenic moiety.

(3) The formation of cyclized sulfones 4a–4f in the reaction of cobaloxime 1 could be explained by the mechanism (Scheme 4) which involves a 5-endo-dig ring closure of 5-phenylpent-4-ynyl radical H to the corresponding cyclopentenyl radical I followed by sulfonyl radical trapping to give 4. This represents the first documented example of such intramolecular ring closure in a sterically unbiased system. Furthermore, we expected that such a mechanism would allow for facile cyclization in the case of 5-trimethylsilylpent-4-ynyl cobaloxime 2, since silicon is known to stabilize the radical or the carbocation β to the silicon atom. The inability of cobaloxime 1 to afford cyclized products during trapping experiments with other heteroatom centred radicals (Eq. 1) may be due to the faster rate of trapping compared with the rate of cyclization of the 5-phenylpent-4-ynyl radical ($k_t > k_c$, Scheme 1). While this remains one of the possibilities, the role of the organometallic fragment $[\text{Co}^{\text{II}}(\text{dmgH})_2\text{Py}]$, if any, in directing such cyclization is worthy of investigation in view of earlier reports from Branchaud and Choi [16].

4. Conclusion

In conclusion, a novel route has been demonstrated towards the formation of a cyclopentene ring system from alkynyl cobaloxime. The synthetic utility of the present work will be appreciated provided the strategy works with other stabilized radical trapping agents, including captodative [17] radicals.

5. Experimental details

All chemicals used were commercial products (Aldrich) and were distilled or recrystallized prior to use. AR grade methylene chloride was refluxed over P_2O_5

under nitrogen and distilled prior to use. All operations were performed by standard Schlenk techniques under dry extra-pure nitrogen. Flash chromatography was performed on silica gel (Acme, 75 μm mesh). Melting points were taken by using a Toshniwal capillary melting point apparatus and are uncorrected. ^1H (200 MHz) and ^{13}C (54 MHz) NMR spectra of all compounds were recorded in CDCl_3 on a Varian Gemini-200 spectrometer. Mass spectra (MS) were recorded at 70 eV by using a Finnigan MAT-1020B instrument while IR spectra were obtained using a Nicolet 740 FTIR spectrometer. Crystal data of compound 4f were collected using a Siemens R3m/v diffractometer ($\text{Mo K}\alpha$) and analysed using Siemens SHELXTL PLUS (VMS) software. The crystal belonged to the orthorhombic system in *Pbca* space group. The final *R* factor was 0.042 ($wR = 0.050$).

5.1. Synthesis of (5-trimethylsilyl)pent-4-ynyl chloride (2a)

BuLi (19.2 ml of 1.6 M in hexane) was added dropwise to a stirred solution of pent-4-ynyl chloride (3 g) in dry THF (20 ml) at -78°C under nitrogen. After 0.5 h a solution of TMSCl (4.12 g) in THF (20 ml) was added dropwise over a period of 0.5 h. The mixture was brought to room temperature (2 h), quenched with cold saturated NH_4Cl and extracted with ether ($3 \times 50\text{ ml}$). The organic layer was dried over MgSO_4 and the solvent removed at reduced pressure to furnish 2a (4.7 g, 92%) as a colourless oil. ^1H NMR: δ 0.1 (s, 9H), 1.92 (qnt, 2H), 2.4 (t, 2H, $J = 8.5\text{ Hz}$), 3.6 (t, 2H, $J = 8.5\text{ Hz}$); IR (CHCl_3) 556(s), 558(vs), 743(s), 845(s), 1066(m), 1170(m), 1190(s), 1248(s), 1385(s), 1395(s), 1485(w), 1564(m), 1772(b), 2164(w), 2903(b) cm^{-1} . Anal. Found: C, 55.25; H, 8.72. $\text{C}_8\text{H}_{15}\text{ClSi}$. Calc.: C, 55.01; H, 8.59%.

5.2. Synthesis of cobaloximes (1–3)

Cobaloximes were prepared by standard protocol [18] from the reaction of $\text{Co}^{\text{I}}(\text{dmgH})_2\text{Py}$ with alkyl halides under nitrogen at 5°C and were recrystallized from ethyl acetate–hexane (1:1 v/v).

5.3. Spectral characteristics of cobaloximes

5.3.1. (5-Phenyl)pent-4-ynyl cobaloxime (1)

^1H NMR: δ 0.94 (m, 2H), 1.6 (t, 2H, $J = 9\text{ Hz}$), 2.15 (s, 12H), 2.3 (t, 2H, $J = 9\text{ Hz}$), 7.3 (m, 5H), 7.41 (t, 2H, $J = 10\text{ Hz}$), 7.73 (t, 1H, $J = 10\text{ Hz}$), 8.6 (d, 2H, $J = 6\text{ Hz}$). Anal. Found: C, 56.45; H, 5.92; N, 13.72. $\text{C}_{21}\text{H}_{30}\text{CoN}_2\text{O}_4$. Calc.: C, 56.36; H, 5.87; N, 13.69%.

5.3.2. (5-Trimethylsilyl)pent-4-ynyl cobaloxime (2)

^1H NMR: δ 0.10 (s, 9H), 1.15 (m, 2H), 1.6 (t, 2H, $J = 9\text{ Hz}$), 2.1 (t, 2H, $J = 7.5\text{ Hz}$), 2.16 (s, 12H), 7.3 (t,

2H, $J = 9$ Hz), 7.7 (t, 1H, $J = 10$ Hz), 8.6 (d, 2H, $J = 6$ Hz). Anal. Found: C, 49.53; H, 6.52; N, 13.65. $C_{21}H_{34}CoN_5O_4Si$. Calc.: C, 49.70; H, 6.70; N, 13.80%.

5.3.3. *Pent-4-ynyl cobaloxime (3)*

1H NMR: δ 1.18 (m, 2H), 1.6 (t, 2H, $J = 8.5$ Hz), 1.85 (s, 1H), 2.05 (m, 2H), 2.15 (s, 12H), 7.3 (t, 2H, $J = 9$ Hz), 7.7 (t, 1H, $J = 10$ Hz), 8.6 (d, 2H, $J = 6$ Hz). Anal. Found: C, 49.82; H, 6.05; N, 16.23. $C_{18}H_{26}CoN_5O_4$. Calc.: C, 49.65; H, 5.97; N, 16.09%.

5.4. General method of photolysis

A solution of cobaloxime (1 mM) in degassed methylene chloride (20 ml) was taken in an all-pyrex double-walled photocatalyser under nitrogen and was externally cooled to $-2^\circ C$ by a thermostated refrigerated circulator (Julabo FC-600). A solution of the organosulfonyl halide (1.5 mM) in deaerated methylene chloride (10 ml) was added to the above with constant stirring and the mixture was subjected to irradiation with a 500 W sun-lamp placed at a distance of 5 cm from the reaction vessel. The reaction was monitored for the cobaloxime by TLC using ethyl acetate as eluent. On completion of the reaction (10–24 h), the reaction mixture was brought to room temperature and was concentrated at reduced pressure before being subjected to flash chromatography. Organic products were isolated by eluting with petroleum ether (60–80°C fraction) followed by methylene chloride in all cases. Inorganic products were eluted with methylene chloride–ethyl acetate (4:1 v/v) mixture. Product sulfones **4a–4f** were further recrystallized from hexane–chloroform (4:1 v/v). No attempts were made to quantify the inorganic products.

5.5. 1H NMR monitoring of the reaction of **1** with $TsCl$

A solution of **1** (50 mg), $TsCl$ (25 mg) and methylene chloride (20 μ l) in $CDCl_3$ (1 ml) was taken in an NMR tube and subjected to three freeze–thaw cycles under nitrogen in a Schlenk-line. The tube was immediately sealed in a flame and placed in a photocatalyser. The methyl signal of $TsCl$ was monitored in a Varian 80 MHz instrument at 15 min intervals for the first 2 h and at 30 min intervals for the next 3 h. The corrected methyl signal integration values I of $TsCl$ with respect to that of methylene chloride were plotted against time (Fig. 1).

5.6. Spectral characteristics of the products

5.6.1. 2-Phenylcyclopentenyl(4-methylphenyl)sulfone (**4a**)

1H NMR: δ 2.0 (m, 2H), 2.39 (s, 3H, 3.9 (m, 4H), 7.2 (dd, 4H), 7.3 (m, 5H); ^{13}C NMR: δ 21.3, 21.6, 35.0, 41.5, 127.3, 127.6, 128.4, 129.2, 135.0, 137.6, 138.3. MS m/z (rel. int.): 298(16), 233(21), 143(13), 142(56),

128(22), 117(100), 115(42), 103(10), 91(14). IR (KBr): 525(m), 583(s), 668(m), 690(m), 1280(m), 1315(vs), 1435(w), 1482(m), 1588(m), 1630(m), 1683(b), 2858(w), 2920(w), 2975(w), 3025(w) cm^{-1} . Anal. Found: C, 72.42; H, 6.10. $C_{18}H_{18}O_2S$. Calc.: C, 72.45; H, 6.08%.

5.6.2. 2-Phenylcyclopentenyl(4-methoxyphenyl) sulfone (**4b**)

M.p. $104^\circ C$. 1H NMR: δ 1.7–2.2 (m, 2H), 2.5–3.0 (m, 4H), 3.71 (s, 3H), 6.7, 7.43 (dd, 4H), 7.2 (m, 5H). Anal. Found: C, 68.90; H, 5.82. $C_{18}H_{18}O_3S$. Calc.: C, 68.78; H, 5.73%.

5.6.3. 2-Phenylcyclopentenyl(4-bromophenyl) sulfone (**4c**)

M.p. $92^\circ C$. 1H NMR: δ 2.0 (m, 2H), 2.9 (m, 4H), 7.15–7.4 (m, 5H), 7.5 (m, 4H); ^{13}C NMR: δ 21.3, 34.9, 41.8, 127.7, 128.1, 128.5, 131.9, 134.7, 137.0, 139.8. MS m/z (rel. int.): 364(20), 362(20), 218(31), 143(15), 142(53), 128(29), 117(100), 115(63), 103(10), 91(42), 77(20). IR (KBr): 548(m), 598(s), 630(s), 696(m), 741(s), 756(m), 1009(m), 1079(m), 1110(w), 1148(vs), 1274(w), 1319(vs), 1441(w), 1470(m), 1573(m), 1595(w), 1632(s), 1678(w), 2960(w), 2945(b), 3060(w) cm^{-1} . Anal. Found: C, 56.30; H, 4.23. $C_{17}H_{15}BrO_2S$. Calc.: C, 56.21; H, 4.16%.

5.6.4. 2-Phenylcyclopentenyl(4-chlorophenyl) sulfone (**4d**)

M.p. $81^\circ C$. 1H NMR: δ 1.7–2.2 (m, 2H), 2.6–3.0 (m, 4H), 6.9–7.6 (m, 9H). Anal. Found: C, 63.52; H, 4.52. $C_{17}H_{15}ClO_2S$. Calc.: C, 63.75; H, 4.68%.

5.6.5. 2-Phenylcyclopentenyl(phenyl) sulfone (**4e**)

1H NMR: δ 1.6–2.2 (m, 2H), 2.2–2.7 (m, 4H), 7.0–7.5 (m, 10H). Anal. Found: C, 71.90; H, 5.68. $C_{17}H_{16}O_2S$. Calc.: C, 71.83; H, 5.63%.

5.6.6. 2-Phenylcyclopentenyl(methyl) sulfone (**4f**)

M.p. $116^\circ C$. 1H NMR: δ 2.0 (m, 2H), 2.58 (s, 3H), 2.9 (m, 4H), 7.3 (m, 5H); ^{13}C NMR: δ 21.4, 34.8, 41.3, 42.2, 127.9, 128.3, 130.0, 135.0, 138.1, 151.9. MS m/z (rel. int.): 222(77), 143(18), 142(67), 128(35), 117(100), 115(67), 103(24), 91(40), 77(10). IR (KBr): 490(m), 520(m), 550(w), 690(s), 768(s), 1008(m), 1100(m), 1142(vs), 1282(vs), 1420(w), 1475(w), 1582(m), 1632(m), 2851(w), 2925(b), 3000(w) cm^{-1} . Anal. Found: C, 64.93; H, 6.37. $C_{12}H_{14}O_2S$. Calc.: C, 64.84; H, 6.35%.

5.6.7. Methanesulfonyl cobaloxime (**6**)

1H NMR: δ 2.38 (s, 6H), 2.5 (s, 3H), 7.2 (m, 2H), 7.7 (m, 1H), 8.15–8.3 (m, 2H). IR (KBr): 696(m), 776(s), 789(s), 1051(s), 1100(s), 1171(vs), 1250(vs), 1277(s), 1439(s), 1499(w), 1560(s), 3341(b) cm^{-1} . Anal.

Found: C, 37.63; H, 5.25; N, 15.72. $C_{14}H_{22}CoN_5O_6S$.
Calc.: C, 37.58; H, 4.92; N, 15.65%.

5.6.8. 4-Methylbenzenesulfonyl cobaloxime (7)

1H NMR: δ 2.18 (bs, 12H), 2.32 (s, 3H), 7.1–7.4 (dd, 4H), 7.25 (m, 2H), 7.7 (m, 1H), 8.35 (m, 2H).
Anal. Found: C, 45.93; H, 5.05; N, 13.25.
 $C_{20}H_{26}CoN_5O_6S$. Calc.: C, 45.88; H, 4.97; N, 13.38%.

5.6.9. 4-Bromobenzenesulfonyl cobaloxime (8)

1H NMR: δ 2.1 (s, 12H), 7.25 (m, 2H), 7.45 (dd, 4H), 7.7 (m, 1H), 8.35 (m, 2H). Anal. Found: C, 38.82; H, 3.85; N, 11.82. $C_{19}H_{23}BrCoN_5O_6S$. Calc.: C, 38.77; H, 3.91; N, 11.90%.

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