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S_H2' Reaction in Organocobaloximes: Synthesis and 1,3-Rearrangement of Exo-Methylene Alicyclic Allyl Sulfones

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Abstract: Photostimulated reactions of cyclopentenylmethyl-, cyclohexenylmethyl- and α-pinenyl cobaloximes with arenesulfonyl halides result in the formation of corresponding exo-methylene cycloalkylsulfones in 82-98% isolated yields. The product formation is rationalized by a radical chain mechanism involving an S_H2' displacement of cobaloxime(II) from organocobaloximes by sulfonyl radical. Reaction under thermal condition, however, provides a mixture of exo-methylene cycloalkylsulfone and its endo-isomer. Independent experiments confirmed that the endo-isomer arises from a facile 1,3-allylic rearrangement of the exo-isomer. From mechanistic and theoretical studies the rearrangement is proposed to involve a [1,3]-sigmatropic migration of sulfonyl group.

INTRODUCTION

After years of deliberation, organometallic compounds are now avowed to undergo free radical chain substitution (S_H2, S_H2') reactions[1]. This is particularly so with organo- tin, mercury, chromium, cobalt, rhodium and iridium compounds. However, little efforts have been paid to exploit these reactions in formulating synthetically viable protocols towards useful organic intermediates. A case in point is the S_H2' substitution reactions in allyl metal complexes. Several groups[2] have demonstrated that these reactions are facile and can be extended to a wide variety of radicals. A single organic product is obtained in all cases which arises from the regiospecific attack of $\dot{X}$ to the terminal olefinic carbon (a γ-attack) in the allyl appendage (Equation1). It is surprising, however, that these demonstrations were

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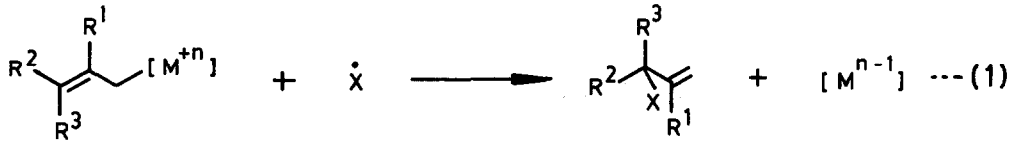


M = Sn, Hg, Co, Rh, Ir, Cr ; $\dot{X}$ = $\dot{C}XYZ$, $\dot{S}Ar$, $\dot{S}O_2Ar$, $\dot{S}O_2Me$ etc.

made with a few select allyl metal complexes only. A synthetically attractive route, on the other hand, must test the generality with respect to a wider spectrum of functionalized allyl-organometallics. In continuation to our earlier work we now present an interesting case wherein exo-methylene alicyclic allyl sulfones, derived from the S_H2' reaction of allyl cobaloximes[3] with arene sulfonyl radicals, undergo facile 1,3-rearrangement to the corresponding endo-isomers. The results clearly highlight the caution that one would require to undertake during the regiochemical assignment in a S_H2' reaction. To our knowledge this also constitutes the first example of 1,3-sulfur shift in allylic sulfones wherein the allylic migration takes place between an exo- to endo-cyclic framework.

RESULTS AND DISCUSSION

Reactions under Photostimulated Condition: Cyclopentenylmethyl cobaloxime 1 is treated with benzene sulfonyl chloride in 1:1.1 molar ratio in dichloromethane under anaerobic photochemical conditions [irradiation with two 200 Watt tungsten lamps] under nitrogen and at 0°C. The reaction is completed within 15 min (TLC inference) to give the organic product as 1-exomethylenecyclopent-2-yl(phenyl) sulfone 2a in 97% isolated yield [Chart 1], the inorganic product being chlorocobaloxime. Similar reactions of 1 with 4-methyl-, 4-bromo-, 4-chloro- and 4-methoxy benzene sulfonyl chlorides give the corresponding 1-exomethylenecyclopent-2-yl sulfones 3a-6a in 83-95% yield. Similar reactions of cyclohexenylmethyl cobaloxime 7 and α-pinenyl cobaloxime 13 affords the corresponding exo-methylene alicyclic allyl sulfones 8a-12a and 14a-18a respectively. Following independent observations characterize the reactions further:

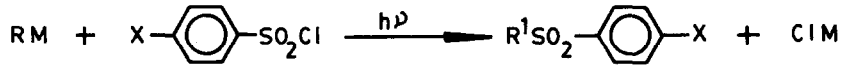
1. The reactions are very slow in the dark, for example a 20% conversion of the parent cobaloxime takes over 48 h.
2. The reactions show concentration dependent induction period. However, once the initiation has begun, the reactions go to completion even without further irradiation.
3. The reaction rate (TLC inference) is drastically lowered by the addition of radical inhibitor like galvinoxyl and is accelerated upon addition of trace amount of dibenzoyl peroxide or $Co^{II}(dmgH)_2Py$.
4. No rearrangement of the parent cobaloximes occurs upon photolysis for 6 h. after which they are recovered back in quantitative yield.

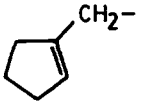
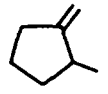
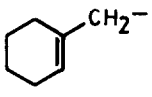
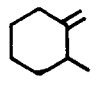
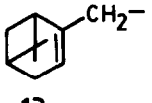
The above results represent one of the most clean and highly efficient S_H2' process ever reported in allyl metal complexes, in general, and cobaloximes, in particular. The products arise from exclusive regiospecific attack of the arene sulfonyl radicals at the γ-allylic carbon of the organocobaloximes. The reactions of α-pinenyl cobaloxime 13 is particularly noteworthy where the γ-attack prevails inspite of much greater steric crowding due to the gem-dimethyl groups at this center. It is believed that such a radical attack is kinetically controlled[1d].The mechanism of the product formation involves a radical chain process, the propagating species being $[Co^{II}]$ and $Ar\dot{S}O_2$ (Scheme 1).

Reactions under Thermal Condition: When the reactions are carried out under thermal condition, the regiospecificity at the first sight, is either lost or totally altered. The results from the reactions of 1, 7 and 13 with tosyl chloride under nitrogen and at various temperature [Chart 2] are summarized below:

1. For reactions carried out at 80°C, the product consists of a mixture of exo-methylene cycloalkyl(tosyl) sulfones and their corresponding endo-isomers.

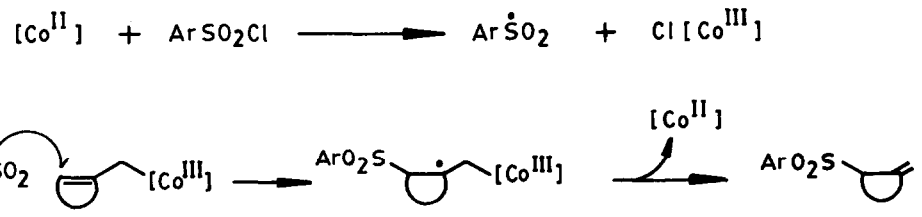
CHART 1: Product from the photostimulated reaction of alicyclic allyl cobaloximes [R-M][a] with arenesulfonyl chlorides



R	X	Time (min.)	R^1	NO.	Yield[b]
 1	H	15		2 a	97
	Me	20		3 a	94
	Br	20		4 a	95
	Cl	40		5 a	92
	OMe	20		6 a	83
 7	H	15		8 a	91
	Me	35		9 a	88
	Br	15		10 a	96
	Cl	30		11 a	82
	OMe	20		12 a	96
 13	H	60		14 a	95
	Me	70		15 a	90
	Br	50		16 a	98
	Cl	90		17 a	95
	OMe	80		18 a	98

a: M = $Co^{III}(dmgH)_2Py.$; b: % Isolated yield w.r.t. RM

Scheme 1



2. In case of cobaloxime 13, formation of a mixture of sulfones 15a and 15b is observed even at 40°C; the endo-isomer predominates over the exo-isomer at higher temperature.
3. Like their photochemical counterpart the thermal reactions also show individual characteristics pertaining to a radical chain mechanism.
4. No rearrangement of the parent cobaloximes occur upon heating under the above conditions. However, at 80°C some decomposition (<20%) occurs leading to ill-defined side-products.
5. Reactions of other arenesulfonyl chlorides show similar behaviour to that of tosyl chloride.

CHART 2 : Products from the thermal reaction of alicyclic allyl cobaloxime [R-M] with tosyl chloride [TsCl].

RM + TsCl $\xrightarrow{\Delta}$ R^1Ts + R^2Ts + CIM

RM	Condn.[a]	Time (min.)	R^1, No.	R^2, No	Ratio[b]	Yield[c]
1	A	25	3a	3b	100 : 0	78
	B	20			100 : 0	86
	C	20			40 : 60	72
7	A	50	9a	9b	100 : 0	70
	B	50			100 : 0	76
	C	45			95 : 5	65
13	A	120	15a	15b	30 : 70	73
	B	120			10 : 90	71
	C	100			5 : 95	62

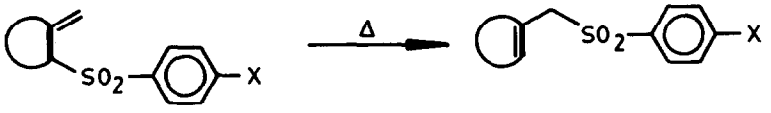
a : A = CH_2Cl_2 / 40°C ; B = $CHCl_3$ / 60°C ; C = CCl_4 / 80° C

b : determined by ^{1}H NMR , c : % isolated yield.

The above results clearly reflect that reactions under thermal condition show a preponderance towards the formation of two isomeric sulfones. Since the mechanistic features of these reaction parallel to their photochemical counterpart, we believe that a similar mechanism as in Scheme 1 is the likely pathway. The endo-isomer may arise from the regiospecific attack of $ArSO_2$ at the α-carbon of the organocobaloximes. Such an attack is totally unprecedented in allyl cobaloximes, however, is known in related propargyl-metal complexes[4]. Factors which often complicate the regiochemical issue in similar reactions are: i) allylic rearrangement of the organometallic complex[1e,2a] and ii) allylic rearrangement of the organic product[5]. Since the parent cobaloximes do not undergo any rearrangement under the reaction conditions, the former possibility is convincingly ruled out. Independent experiments confirmed that the endo-isomer arises from thermal rearrangement of the exo-isomer. Thus, when a solution exo-methylene cyclopent-2-yl(phenyl) sulfone 2a in hexane (0.2 mML^{-1}) is refluxed under nitrogen for 5 min, the corresponding cyclopentenylmethyl(phenyl) sulfone 2b is isolated in quantitative yield (Chart 3). Substitution in the

phenyl ring of the arenesulfonyl chloride does not alter the rate of the reaction to a significant extent as shown in the rearrangement of 3a-6a to 3b-6b. In sharp contrast, cycloalkane ring size does influence the temperature of rearrangement. This is exemplified in the case of exo-methylenecyclohex-2-yl(phenyl) sulfone 8a which undergoes 70% rearrangement to 8b when refluxed in CCl_4 (80°C) for 25 h; a total conversion requires heating at 140°C for 6h. Similar behaviour is shown in the conversion of 9a-10a to 9b-10b. On the other hand, β-pinenyl(phenyl) sulfones 14a-18a undergo very facile rearrangement to the corresponding endo-isomers 14b-18b even in refluxing dichloromethane or n-hexane.

CHART 3 : Thermal rearrangement of Exo-methylene alicyclic allyl sulfones to Endo-isomers.



	X	No.	Condn.[a]	Time (min.)	Pdt. No.	% Conv.[b]
	H	2 a	A	720	2 b	0
			B	5	2 b	100
	Me	3 a	B	7	3 b	100
	Br	4 a	B	2	4 b	100
	Cl	5 a	B	4	5 b	100
	OMe	6 a	B	10	6 b	100
	H	8 a	C	300	8 b	70
	Me	9 a	C	360	9 b	65
	Br	10 a	C	360	10 b	82
	H	14 a	A	15	14 b	12
			B	3	14 b	100
	[c]Me	15 a	A	20	15 b	30
	[c]Br	16 a	A	10	16 b	22
	[c]Cl	17 a	A	15	17 b	20
	[c]OMe	18 a	A	15	18 b	15

a. A = CH_2Cl_2/40°C ; B = n-C_6H_{14}/69°C ; C = CCl_4/80°C, b. determined by ^1H NMR, c. 100% conv. to endo-isomer within 5min under condn. B.

MECHANISTIC REFLECTIONS ON THE 1,3-REARRANGEMENT

To date 1,3-sulfur shift in allylic sulfones has been viewed in terms of three distinct mechanisms[6-9].

(a) Radical chain mechanism for rearrangement under thermal or photostimulated condition.

(b) An ion-pair mechanism for acid catalized rearrangement.
(c) Radical-anion ($S_{RN}1$) mechanism for reactions done in presence of excess of sulfonate salt.

For the 1,3-allylic rearrangements in the present study, mechanism (b) and (c) can be conveniently ruled out since the experiments were conducted in absence of acid or sulfonate salt as catalyst. One is therefore left with the following two mechanistic plausibilities:

i. a thermally assisted 'associative radical' or 'radical-chain' pathway
ii. a [1,3]- or [2,3]-sigmatropic rearrangement mechanism.

In all previous cases of thermal rearrangements in allylic sulfones and sulfides it was observed that diffused day light is mandatory to initiate the reactions. Furthermore, the reactions could be catalyzed by irradiating with a sun-lamp or by adding dibenzoyl peroxide; and are retarded when reactions were done in dark or in presence of hydroquinone as radical inhibitor. In view of the above, several independent experiments were conducted as highlighted in Table 1 taking the rearrangement of 9a to 9b as a typical example. The following conclusions can be drawn from these experiments.

1. The rearrangements are temperature specific; in case of 9a the minimum temperature required for rearrangement is 80°C.
2. Similar product distribution is observed for reactions conducted in dark, in diffused light and in presence of one mol. equiv. of hydroquinone.
3. No rearrangement takes place upon irradiation for extended hours at low temperature.

From these results a free radical mechanism for 1,3-rearrangement in our systems seems inappropriate. To further strengthen this hypothesis cross- over experiments were carried out. As can be seen from Table 2, in all three examples no cross-over product could be detected. We believe, therefore, that sigmatropic rearrangements could be the probable pathway for the 1,3-sulfur shift observed in our systems. A [2,3]-sigmatropic migration[5d] is ruled out in view of the experimental observations that (i) base hydrolysis of 2a and 9a does not lead to the corresponding alcohols, and (ii) the S=O stretching frequencies in the FT-IR spectra of the exo-methylene alicyclic sulfones are nearly identical to that of the endo-cyclic

Table 1: Rearrangement of 9a to 9b under various conditions.

Condition	Temperature(°C)	Time (h)	% Conversion[a]
CH_2Cl_2	40	6	0
Hexane	69	6	0
CCl_4	80	6	65
Toluene	111	6	91
Xylene	143	6	100
CH_2Cl_2, $h\nu$[b]	20	6	0
CCl_4, dark[c]	80	8	77
CCl_4, HQ[d]	80	8	81

a. by ^1H NMR; b. 500 Watt sunlamp; c. aluminium foil wrapped; d. in presence of 1 mol. equiv. of hydroquinone.

Table 2: [1,3]-Allylic Rearrangement: Cross-Over Experiments

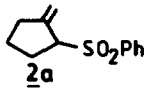
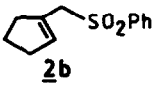
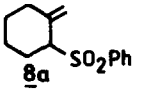
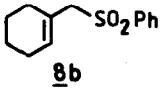
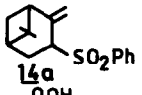
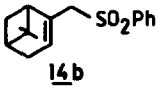
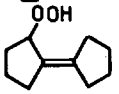
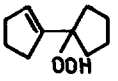
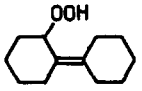
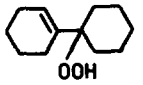
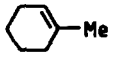
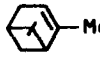
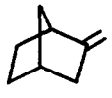
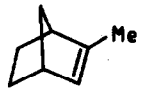
Reactant (mol. ratio)	Temperature(°C)	Time(h)	Product(mol. ratio)
2a + 9a (1:1)	111	8	2b + 9b (1:1)
2a + 17a (1:1)	69	2	2b + 17b (1:1)
2a + TsCl (1:1)	69	2	2b + TsCl (1:1)

isomers. Hence, the thermal rearrangements are likely to occur through the [1,3]-sigmatropic migration of sulfonyl group.

THEORETICAL INTERPRETATION

To gain further insight into the mechanism of [1,3]-sigmatropic shift, molecular mechanics (MMX) calculation was carried out on the exo- and endo-cyclic isomers. The results show (Table 3) that in all cases steric energy of the exo-isomer is higher than the corresponding endo-isomer; the latter, therefore, is thermodynamically more favoured. Furthermore, substituents (Cl, Br, Me, OMe) in the para-position

Table 3: MMX steric energies (K cal mol^{-1}) of exo/endo isomers

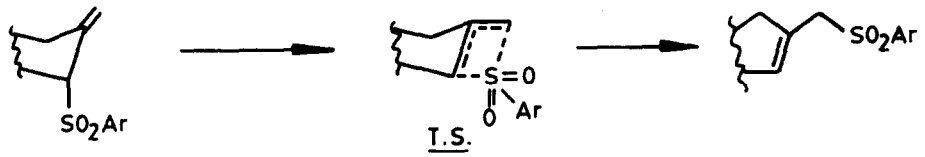
Entry	Exo-isomer	E_s	ϕ (°)[a]	Endo-isomer	E_s	ΔE_s
1	 2a	22.4	55	 2b	18.8	3.6
2	 8a	19.6	98	 8b	15.3	4.3
3	 14a	57.1	31	 14b	49.5	7.6
4[b]		21.8	—		20.4	1.4
5[b]		21.4	—		17.6	3.8
6		10.8	—		7.3	3.5
7		6.0	—		3.8	2.2
8		43.7	—		38.7	5.0
9		23.6	—		25.3	-1.7

a. refers to dihedral angle ∠C=C-C-S in the exo-isomer ; b. ref. 5b

of the phenyl ring in the sulfones do not cause any noticeable change in the ΔE_s values as compared to those in the unsubstituted cases. Similar calculations[56] on acyclic allyl hydroperoxides also corroborate the above view (entry 4 and 5).

Theoretical as well as experimental studies deliberating on the stability of exo-cyclic ring systems are well documented in literature. It is generally understood,[10,11] that between the five and six member exo/endo pairs, the endo arrangement is more stable partly due to the fact that tri-substituted olefins have lower energy and partly due to the poor torsional arrangement in the exocyclic case. However, experimental observations[12] show that in norbornene ring systems the exo- arrangement is favoured over the endo-arrangement. In light of the above, MMX calculations were extended to exo-methylene cyclopentane, exo-methylene cyclohexane, exo-methylene norbornane, β-pinene and their endo-cyclic analogs (Table 3). The results clearly reflect that even in their basic core-motiff, the endo-isomers are more stable than the exo-isomers; 2-methyl norbornene being the only exception. The experimental order of rearrangement reactivity i.e. 8a→8b<2a→2b<14a→14b is in apparent correlation with the dihedral angle Φ values (Table 3). The dihedral angle Φ in 8a approximates to 98°, thereby indicating that the arenesulfonyl group favours a near-axial orientation[13]. This value is significantly lowered to 55° and 31° in 2a and 14a respectively. The influence of Φ becomes obvious from the mechanism of the 1,3-allylic rearrangement which is believed to involve a four member cyclic transition state (Scheme 2). A lower Φ value in the exo-isomer indicates ease of formation of T.S.; that is a lowering in the enthalpy of activation.

Scheme 2



In conclusion, we have shown that a clean and efficient S_H2' reaction can be manifested in alicyclic allyl cobaloximes under photochemical condition; the regiospecificity of radical attack being at the expected γ-position. The apparent breakdown in regiospecificity in the thermal reactions, wherein two isomers are formed, is in fact due to a concurrent [1,3]-sigmatropic rearrangement of the S_H2' derived sulfone which can be effected even at 40°C. While sulfones in general are known[14] to mediate various transformations leading to the syntheses of natural products, the 1,3-rearrangement in allylic sulfones has earned distinct focus only recently[5,6]. In light of this, the present methodology holds promise towards the synthesis and 1,3-rearrangement of allyl sulfones under very mild conditions.

EXPERIMENTAL

All reactions were performed under an inert atmosphere of extrapure nitrogen. Organosulfonyl chlorides were recrystallized or distilled prior to use. Dichloromethane was distilled over P_2O_5 and stored over molecular sieve 4Å. All other solvents and reagents were purified and distilled when necessary following standard prescriptions. Melting points were determined using a Fischer-John's instrument and are uncorrected. ^{1}H NMR spectra ($CDCl_3$) were obtained on 80 MHz Brucker, 200 MHz Varian Gemini and 400 MHz Varian XL-400 spectrometers. Mass spectra (MS) were recorded at 70eV by using a VG Micromass 7070F or a Finnigan MAT-1020B instruments. Principal molecular fragments alongwith their relative abundance are reported. IR spectra were obtained by using Perkin-Elmer 3220, 850 and Nicolet 740 FTIR spectrometers, the sulfonyl stretching frequencies ($\bar{\nu}_{max}$, cm^{-1}) are reported. Electronic spectra were recorded in MeOH solution on a Carry-170 and Simadzu UV-190 spectrometers; absorbance maxima (λ_{max}, nm) are reported.

Synthesis of Cyclopentenylmethyl cobaloxime 1, cyclohexenylmethyl cobaloxime 7, and α-pinenyl cobaloxime 13: Cobaloximes 1, 7, 13 were prepared from the reaction of $Co^I(dmgH)_2Py$ and the respective halides[15,16] and are purified by flash chromatography on silica gel using dichloromethane as eluent. ^{1}H NMR ($CDCl_3$): 1: 1.85-2.80 (m, 6H, cy-pent), 2.13 (s, 2H, dmgH), 2.55 (s, 2H, CH_2-Co),

5.40 (s, ^{1}H, :CH), 7.27; 7.61; 8.28 (m, Py) 7: 1.60-1.95 (m, 6H, cy-hex), 2.14 (s, 2H, dmgH), 2.33 (t, 2H, CH_2-C:), 2.46 (s, 2H, CH_2-Co), 5.28 (s, ^{1}H, :CH), 7.30; 7.72; 8.57 (m, 5H, Py). 13: 0.71; 1.24 (s, 6H, gem-CH_2), 0.80-2.02 (m, 12H, cy-alk), 2.12 (s, 12H, dmgH), 2.31 (s, 2H, CH_2-Co), 5.40 (s, ^{1}H, :CH), 7.30; 7.63; 8.61 (m, 5H, Py).

General Method of Photolysis: A solution of organocobaloxime (2.2 mM) in degassed dichloromethane (50 mL) was taken in an all pyrex double walled photocatalizer under nitrogen and was externally cooled to 0°C by a thermostated refrigerated circulator (Julabo UC-20). A solution of the arenesulfonyl chloride (2.4 mM) in deaerated dichloromethane (10 mL) was added to the above with constant stirring and the mixture was subjected to irradiation with two 200W tungsten lamps placed at a distance of 5 cm apart from the reaction vessel. The reaction was monitored for organocobaloxime by TLC on silicagel using ethylacetate as eluent. Upon completion (15-90 min), the mixture was brought to room temperature and was concentrated at reduced pressure before subjecting to flash chromatography. Exomethylene cycloalkyl(phenyl) sulfone was eluted with dichloromethane.

Representative Method of Thermolysis: Exo-methylene cyclopent-2-yl (phenyl) sulfone 2a (22 mg, 1 mM) in hexane (5 mL) was refluxed for 5 min. after which solvent was stripped off in vacuo to afford cyclopetenylmethyl (phenyl) sulfone 2b in quantitative yield vide ^{1}H NMR. Recrystallization of this product was further carried out from hexane.

Spectral Characteristics of Products:

Exomethylenecyclopent-2-yl(phenyl) sulfone 2a: White solid. m.p. 93°C; ^{1}H NMR: 1.31-2.50 (m, 6H, cy-pent), 3.99 (m, ^{1}H, CH-SO_2), 5.11 (d, ^{1}H, :CH_2), 7.42-8.04 (m, 5H, arom); MS (m/z): 222 (4.4), 143 (19.6), 81 (100), 80 (99.5), 79 (73); IR (KBr): 1120, 1139, 1152, 1303; UV: 216, 251, 257, 263, 270. Anal. calcd. for $C_{12}H_{14}O_2S$: C, 64.82; H, 6.35. Found: C, 64.61; H, 6.27.

Exomethylenecyclopent-2-yl(4-methyl phenyl) sulfone 3a: White solid; m.p. 64°C; ^{1}H NMR: 1.54-2.53 (M, 6H, cy-pent), 2.44 (s, 3H, CH_2), 3.97 (m, ^{1}H, CH-SO_2), 5.13 (d, ^{1}H, :CH_2), 5.24 (d, ^{1}H, :CH_2), 7.25-7.88 (m, 5H, arom); MS (m/z): 236 (1.9), 157 (40.1), 91 (36.9), 81 (100), 80 (99.1), 79 (61.6); IR (KBr): 1133, 1154, 1298, 1312; UV: 254, 261, 263, 275. Anal. Calcd. for C13H14O_2S: C, 66.05; H, 6.29. Found: C, 66.10; H, 6.18.

Exomethylenecyclopent-2-yl(4-bromo phenyl) sulfone 4a: White solid; m.p. 69°C; ^{1}H NMR: 1.30-2.47 (m, 6H, cy-pent), 3.97 (m, ^{1}H, CH-SO_2), 5.15 (d, ^{1}H, :CH_2), 7.78 (s, 4H, arom); MS (m/z): 302 (2.9), 300 (2.9), 221 (1.5), 155 (5.5), 81 (100), 80 (84.0), 79 (43.2); IR (KBr): 1139, 1172, 1295, 1309; UV: 228, 266, 273. Anal. Calcd. for $C_{12}H_{13}BrO_2S$: C, 47.83; H, 4.35. Found: C, 48.01; H, 4.18.

Exomethylenecyclopent-2-yl(4-chloro phenyl) sulfone 5a: White solid; m.p. 53°C; ^{1}H NMR: 1.50-2.47 (m, 6H, cy-pent), 3.92 (m, ^{1}H, CH-SO_2), 5.15 (d, ^{1}H, :CH_2), 5.25 (d, ^{1}H, :CH), 7.44-8.03 (m, 5H, arom); MS (m/z): 256 (0.7), 177 (1.6), 111 (10.0), 81 (5.0), 80 (100), 79 (52.5); IR (KBr): 1121, 1144, 1304; UV: 233, 267, 275. Anal. Calcd. for $C_{12}H_{13}ClO_2S$: C, 56.12; H, 5.10. Found: C, 56.66; H, 5.20.

Exomethylenecyclopent-2-yl(4-methoxy phenyl) sulfone 6a: Colorless oil. ^{1}H NMR: 1.432.44 (m, 6H, cy-pent), 3.89 (s, 3H, OCH_2), 3.94 (m, ^{1}H, CH-SO_2), 5.13 (d, ^{1}H, :CH_2), 5.22 (d, ^{1}H, :CH_2), 6.94-7.10 (m, 4H, arom); MS (m/z): 252 (0.3), 188 (15.6), 173 (22.2), 81 (7.1), 80 (100), 79 (71.4); IR (neat): 1144, 1178, 1297, 1315; UV: 240, 265, 271. Anal. Calcd. for $C_{13}H_{16}O_3S$: C, 61.86; H, 6.39. Found: C, 61.70; H, 6.22.

Exomethylenecyclohex-2-yl(phenyl) sulfone 8a: White solid; m.p. 123°C; ^{1}H NMR: 1.14-2.97 (m, 8H, cy-hex), 3.69 (m, ^{1}H, CH-SO_2), 4.39 (s, ^{1}H, :CH_2), 4.92 (s, ^{1}H, :CH_2), 7.34-7.99 (m, 5H, arom); MS (m/z): 236 (1.9), 173 (4.9), 95 (100), 94 (70.3); IR (KBr): 1129, 1143, 1155, 1290, 1320; UV: 216, 252, 258, 264, 271. Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.05; H, 6.82. Found: C, 66.01, H, 6.73.

Exomethylenecyclohex-2-yl(4-methyl phenyl) sulfone 9a: White solid; m.p. 70°C; ^{1}H NMR: 1.26-2.88 (m, 8H, cy-hex), 2.50 (s, 3H, CH_2), 3.75 (m, ^{1}H, CH-SO_2), 4.53 (s, ^{1}H, :CH_2), 5.04 (s, ^{1}H, :CH_2), 7.34-8.04

(m, 5H, arom); MS (m/z): 250 (0.3), 186 (0.8), 95 (100), 94 (100), 93 (23.7); IR (KBr): 1121, 1139, 1157, 1165, 1290, 1305, 1315; UV: 225, 253, 260, 264, 271. Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 67.15; H, 7.25. Found: C, 67.37, H, 7.18.

Exomethylenecyclohex-2-yl(4-bromo phenyl) sulfone 10a: White solid; m.p. 81°C; ^{1}H NMR: 1.16-2.82 (m, 8H, cy-hex), 3.72 (m, ^{1}H, CH-SO_2), 4.49 (s, ^{1}H, :CH_2), 5.00 (s, ^{1}H, :CH_2), 7.81 (s, 4H, arom); MS (m/z): 317 (3.3), 222 (15.0), 220 (15.0), 156 (7.5), 95 (100), 94 (40.0), 93 (53.5); IR (KBr): 1131, 1144, 1156, 1297, 1300, 1307; UV: 235, 267, 270. Anal. Calcd. for $C_{13}H_{15}BrO_2S$: C, 49.51; H, 4.79. Found: C, 49.81; H, 4.60.

Exomethylenecyclohex-2-yl(4-chloro phenyl) sulfone 11a: White solid; m.p. 72°C; ^{1}H NMR: 1.16-3.10 (m, 8H, cy-hex), 3.75 (m, ^{1}H, CH-SO_2), 4.50 (s, ^{1}H, :CH_2), 5.02 (s, ^{1}H, :CH_2), 7.51-8.17 (m, 4H, arom); MS (m/z): 271 (0.2), 177 (36.3), 111 (20.0), 95 (100), 94 (37.5), 93 (10.0); IR (KBr): 1128, 1140, 1149, 1305; UV: 228, 265, 274. Anal. Calcd. for $C_{13}H_{15}ClO_2S$: C, 57.64; H, 5.58. Found: C, 57.50; H, 5.58.

Exomethylenecyclohex-2-yl(4-methoxy phenyl) sulfone 12a: White solid; m.p. 64°C; ^{1}H NMR: 1.16-2.72 (m, 8H, cy-hex), 3.86 (s, 3H, OCH_2), 3.60 (m, ^{1}H, CH-SO_2), 4.38 (s, ^{1}H, :CH_2), 4.87 (s, ^{1}H, :CH_2), 6.93 (d, J=10Hz, 2H, arom), 7.71 (d, J=10Hz); MS (m/z): 266 (0.3), 202(10.7), 173 (46.0), 107(9.6), 95 (100), 94 (88.2); IR (KBr): 1132, 1143, 1153, 1297, 1307, 1318; UV: 240, 264, 277. Anal. Calcd. for $C_{14}H_{18}O_3S$: C, 63.11; H, 6.81. Found: C, 63.43, H, 6.79.

β-Pinenyl(phenyl) sulfone 14a: White solid; m.p. 110°C; ^{1}H NMR: 0.67 (s, 3H, gem-CH_2), 1.17 (s, 3H, gem-CH_2), 1.36-2.56 (m, 6H, cy-alk), 3.90-4.10 (m, ^{1}H, CH-SO_2), 4.93 (d, J= 6 Hz, ^{1}H, :CH_2), 5.78 (d, J= 6 Hz, ^{1}H, :CH_2), 7.56-7.96 (m, 5H, arom); MS (m/z): 276 (3.0), 141 (5.1), 135 (44.9), 119 (43.6), 106 (29.5), 91 (100); IR (KBr): 1125, 1155, 1161, 1308, 1314; UV: 216, 259, 265, 272. Anal. Calcd. for $C_{16}H_{20}O_2S$: C, 69.51; H, 7.29. Found: C, 70.03; H, 7.23.

β-Pinenyl(4-methyl phenyl) sulfone 15a: Colourless oil; ^{1}H NMR: 0.66 (s, 3H, gem-CH_2), 1.15 (s, 3H, gem-CH_2), 1.50-2.55 (m, 6H, cy-alk), 2.38 (s, 3H, CH_2), 3.80-4.30 (m, ^{1}H, CH-SO_2), 4.93 (d, J= 6 Hz, ^{1}H, :CH_2), 5.80 (d, J= 6 Hz, ^{1}H, :CH_2), 7.30-7.57 (m, 4H, arom); MS (m/z): 290 (2.1), 155 (14.1), 135 (35.9), 119 (34.6), 106 (26.9), 91 (100); IR (KBr): 1148, 1155, 1161, 1295, 1308, 1320; UV: 226, 245, 262, 272. Anal. Calcd. for $C_{17}H_{22}O_2S$: C, 70.29; H, 7.63. Found: C, 70.05; H, 7.58.

β-Pinenyl(4-bromo phenyl) sulfone 16a: White solid; m.p. 103°C; ^{1}H NMR: 0.70 (s, 3H, gem-CH_2), 1.21 (s, 3H, gem-CH_2), 1.56-2.68 (m, 6H, cy-alk), 3.94-4.20 (m, ^{1}H, CH-SO_2), 4.95 (d, J= 6 Hz, ^{1}H, :CH_2), 5.81 (d, J= 6 Hz, ^{1}H, :CH_2), 7.76 (m, 4H, arom); MS (m/z): 355 (0.4), 353 (0.4), 219 (2.4), 220 (2.4), 135 (13.2), 119 (20.5), 106 (15.5), 91 (100); IR (KBr): 1125, 1135, 1168, 1314; UV: 235, 255, 265, 277. Anal. Calcd. for $C_{16}H_{19}BrO_2S$: C, 54.06; H, 5.39. Found: C, 54.21; H, 5.22.

β-Pinenyl(4-chloro phenyl) sulfone 17a: White solid; m.p. 69-71°C; ^{1}H NMR: 0.67 (s, 3H, gem-CH_2), 1.20 (s, 3H, gem-CH_2), 1.60-2.67 (m, 6H, cy-alk), 3.85-4.40 (m, ^{1}H, CH-SO_2), 4.97 (d, J= 6 Hz, ^{1}H, :CH_2), 5.80 (d, J= 6 Hz, ^{1}H, :CH_2), 7.23-7.93 (m, 4H, arom); MS (m/z): 310 (0.3), 175 (2.6), 135 (25.6), 119 (33.4), 106 (18.0), 91 (100); IR (KBr): 1125, 1150, 1165, 1312, 1321, 1328; UV: 225, 252, 271, 279. Anal. Calcd. for $C_{16}H_{19}ClO_2S$: C, 61.80; H, 6.16. Found: C, 70.14; H, 6.16.

β-Pinenyl(4-methoxy phenyl) sulfone 18a: White solid; m.p. 74°C; ^{1}H NMR: 0.66 (s, 3H, gem-CH_2), 1.20 (s, 3H, gem-CH_2), 1.32-2.55 (m, 6H, cy-alk), 3.89 (s, 3H, OCH_2), 4.16-4.24 (m, ^{1}H, CH-SO_2), 5.02 (d, J= 6 Hz, ^{1}H, :CH_2), 5.88 (d, J= 6 Hz, ^{1}H, :CH_2), 6.92-7.88 (m, 4H, arom); MS (m/z): 306 (0.3), 171 (20.5), 135 (79.5), 119 (53.9), 106 (30.8), 91 (100); IR (KBr): 1134, 1144, 1300, 1318; UV: 241, 258, 267, 276. Anal. Calcd. for $C_{17}H_{22}O_3S$: C, 66.62; H, 7.24. Found: C, 66.87; H, 7.20.

Cyclopentenylmethyl(phenyl) sulfone 2b: ^{1}H NMR: 1.65-2.42 (m, 6H, cy- pent), 3.90 (s, 2H, CH_2-SO_2), 5.56 (bs, ^{1}H, :CH), 7.45-7.85 (m, 5H, arom); MS (m/z): 222 (6.3), 81 (100); IR (KBr): 751, 832, 1141, 1150, 1308, 1680, 2951. Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.82; H, 6.35. Found: C, 64.62; H, 6.28.

Cyclopentenylmethyl(4-methyl phenyl) sulfone 3b: ^{1}H NMR: 1.30-2.70 (m, 6H, cy-pent), 2.45 (s, 3H, CH_2), 3.78 (s, 2H, CH_2-SO_2), 5.50 (bs, ^{1}H, :CH), 7.28-7.50 (m, 2H, arom), 7.60-7.90 (m, 2H, arom);

MS (m/z): 236 (2.5), 81 (100); IR (KBr): 760, 828, 1145, 1161, 1312, 1676, 2995. Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.05; H, 6.29. Found: C, 66.01; H, 6.23.

Cyclopentenylmethyl(4-bromo phenyl) sulfone 4b: ^{1}H NMR: 1.63-2.53 (m, 6H, cy-pent), 3.76 (s, 2H, CH_2-SO_2), 5.40 (bs, ^{1}H, :CH), 7.68 (s, 4H, arom); MS (m/z): 302 (2.9), 81 (100); IR (KBr): 811, 1142, 1170, 1305, 1313, 1659, 2940. Anal. Calcd. for $C_{12}H_{13}BrO_2S$: C, 47.83; H, 4.35. Found: C, 48.01; H, 4.44.

Cyclopentenylmethyl(4-chloro phenyl) sulfone 5b: ^{1}H NMR: 1.58-2.53 (m, 6H, cy-pent), 3.76 (s, 2H, CH_2-SO_2), 5.43 (bs, ^{1}H, :CH), 7.50-8.04 (m, 4H, arom); MS (m/z): 256 (0.8), 81 (100); IR (KBr): 748, 802, 1147, 1310, 1665, 2935. Anal. Calcd. for $C_{13}H_{15}ClO_2S$: C, 56.12; H, 5.10. Found: C, 56.45; H, 5.22.

Cyclopentenylmethyl(4-methoxy phenyl) sulfone 6b: ^{1}H NMR: 1.53-2.53 (m, 6H, cy-pent), 3.84 (s, 3H, OCH_2), 3.76 (s, 2H, CH_2-SO_2), 5.46 (bs, ^{1}H, :CH), 6.80-7.06 (m, 2H, arom), 7.56-7.91 (m, 2H, arom); MS (m/z): 252 (1.1), 81 (100); IR (neat): 795, 1152, 1178, 1302, 1318, 1681, 3007. Anal. Calcd. for $C_{13}H_{16}O_3S$: C, 61.86; H, 6.39. Found: C, 61.75; H, 6.22.

Cyclohexenylmethyl(phenyl) sulfone 8b: ^{1}H NMR: 1.26-2.40 (m, 8H, cy- hex), 3.53 (s, 2H, CH_2-SO_2), 5.30 (bs, ^{1}H, :CH), 7.36-7.90 (m, 5H, arom); MS (m/z): 236 (1.8), 95 (100); IR (neat): 752, 805, 1134, 1162, 1295, 1315, 1671, 2950. Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.05; H, 6.29. Found: C, 65.82; H, 6.35.

Cyclohexenylmethyl(4-methyl phenyl) sulfone 9b ^{1}H NMR: 1.03-2.01 (m, 8H, cy-hex), 2.32 (s, 3H, CH_2), 3.56 (s, 2H, CH_2-SO_2), 5.30 (bs, ^{1}H, :CH), 7.23 (m, 2H, arom), 7.66 (m, 2H, arom); MS (m/z): 205 (0.9), 95 (100); IR (neat): 756, 815, 1148, 1176, 1303, 1315, 1673, 2901. Anal. Calcd. for $C_{14}H_{18}O_2S$: C, 67.15; H, 7.25. Found: C, 67.20; H, 7.11.

Cyclohexenylmethyl(4-bromo phenyl) sulfone 10b: ^{1}H NMR: 1.22-2.50 (m, 8H, cy-hex), 3.45 (s, 2H, CH_2-SO_2), 5.21 (bs, ^{1}H, :CH), 7.62 (m, 5H, arom); MS (m/z): 222 (1.2), 220 (1.2), 95 (100); IR (neat): 744, 810, 1152, 1285, 1320, 1665, 2956. Anal. Calcd. for $C_{13}H_{15}BrO_2S$: C, 49.51; H, 4.79. Found: C, 49.66; H, 4.92.

α-Pinenyl(phenyl) sulfone 14b: ^{1}H NMR: 0.83 (s, 3H, gem-CH_2), 1.26 (s, 3H, gem-CH_2), 1.50-2.63 (m, 6H, cy-alk), 3.60 (s, 2H, CH_2-SO_2), 5.30 (bs, ^{1}H, :CH), 7.30-7.95 (m, 5H, arom); MS (m/z): 276 (3.9), 91 (100); IR (KBr): 762, 820, 1147, 1162, 1315, 1671, 3010. Anal. Calcd. for $C_{16}H_{20}O_2S$: C, 69.51; H, 7.29. Found: C, 69.38; H, 7.44.

α-Pinenyl(4-methyl phenyl) sulfone 15b: ^{1}H NMR: 0.80 (s, 3H, gem-CH_2), 1.25 (s, 3H, gem-CH_2), 1.38 (s, 3H, CH_2), 1.46-2.60 (m, 6H, cy-alk), 3.58 (s, 2H, CH_2-SO_2), 5.28 (bs, ^{1}H, :CH), 7.0-7.33 (m, 2H, arom), 7.45-7.80 (m, 2H, arom); MS (m/z): 290 (2.9), 91 (100); IR (KBr): 820, 1152, 1159, 1305, 1320, 1671, 2989. Anal. Calcd. for $C_{17}H_{22}O_2S$: C, 70.29; H, 7.63. Found: C, 70.33; H, 7.40.

α-Pinenyl(4-bromo phenyl) sulfone 16b: ^{1}H NMR: 0.82 (s, 3H, gem-CH_2), 1.28 (s, 3H, gem-CH_2), 1.28-2.65 (bm, 6H, cy-alk), 3.65 (s, 2H, CH_2-SO_2), 5.32 (bs, ^{1}H, :CH), 7.6 (m, 4H, arom); MS (m/z): 355 (0.3), 3.53 (0.4), 91 (100); IR (KBr): 798, 1131, 1152, 1302, 1318, 1673, 2980. Anal. Calcd. for $C_{16}H_{19}BrO_2S$: C, 54.06; H, 5.39. Found: C, 53.89; H, 5.52.

α-Pinenyl(4-chloro phenyl) sulfone 17b: ^{1}H NMR: 0.80 (s, 3H, gem-CH_2), 1.26 (s, 3H, gem-CH_2), 1.60-2.60 (m, 6H, cy-alk), 3.63 (s, 2H, CH_2-SO_2), 5.28 (bs, ^{1}H, :CH), 7.23-7.93 (m, 4H, arom); MS (m/z): 310 (0.5), 91 (100); IR (KBr): 751, 802, 1115, 1150, 1155, 1309, 1323, 1669, 2980, 3015. Anal. Calcd. for $C_{16}H_{19}$, ClO_2S: C, 61.80; H, 6.16. Found: C, 61.89; H, 6.22.

α-Pinenyl(4-methoxy phenyl) sulfone 18b: ^{1}H NMR: 0.82 (s, 3H, gem-CH_2), 1.27 (s, 3H, gem-CH_2), 1.32-2.55 (m, 6H, cy-alk), 3.74 (s, 2H, CH_2-SO_2), 3.89 (s, 3H, OCH_2), 5.34 (bs, ^{1}H, :CH), 6.92-7.16 (m, 2H, arom), 7.68- 7.88 (m, 2H, arom); MS (m/z): 306 (0.3), 91 (100); IR (KBr): 753, 805, 1141, 1162, 1310, 1320, 1678, 2970. Anal. Calcd. for $C_{17}H_{22}O_3S$: C, 66.62; H, 7.24. Found: C, 66.80; H, 7.11.

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REFERENCES & NOTES

1. a. Giese, B. Radical in Organic Synthesis: Formation of Carbon-Carbon Bonds, Pergamon Press, Oxford, 1986; b. Ramaiah, M. Tetrahedron 1987, 43, 3541; c. Curran, D.P. Synthesis 1988, 417, 489; d. Johnson, M.D. Acc. Chem. Res. 1983, 16, 343; e. Davies, A.G.; Roberts, B.P. Acc. Chem. Res. 1972, 387; f. Pattenden, G. Chem. Soc. Rev. 1988, 17, 361.

2. a. Russell, G.A.; Herold, L.L. J. Org. Chem. 1985, 50, 1037. b. Russell, G.A.; Ngoviwatchai, P.; Wu, Y.W. J. Am. Chem. Soc. 1989, 111, 4921; c. Crease, A.E.; Gupta, B.D.; Johnson, M.D.; Moorhouse, S. J. Chem. Soc. Dalton Trans. 1978, 1821; d. Ashcroft, M.R.; Bougeard, P.; Bury, A.; Cooksey, C.J.; Johnson, M.D. J. Organometal. Chem. 1985, 289, 403; e. Roy, S.; Gupta, B.D.; Chaklanobis, S. J. Organometal. Chem. 1984, 269, 201.

3. Organocobaloxime is the trivial name for organobis(dimethyl glyoximato)(pyridine) Cobalt(+3) complexes, $RCo^{III}(dmgH)_2Py$, where, R= organic ligand, dmgH= dimethylglyoxime monoanion and Py= pyridine.

4. Gupta, B.D.; Roy, S. J. Chem. Soc. Perkin Trans. 2. 1988, 1377.

5. a. Betancor, C.; Carrau, R.; Francisco, C.G.; Suarez, E. Tetrahedron Lett. 1986, 27, 4783; b. Dang, H.-Shan.; Davies, H.G.; Davison, I.G.E.; Schiesser, C.H. J. Org. Chem. 1990, 55, 1432; c. Warren, S. Acc. Chem. Res. 1978, 11, 401; d. Knight, D.J.; Whithan, G.H.; Willams, J.G. J. Chem. Soc. Perkin Trans. 1 1987, 2149; e. Padwa, A.; Bullock, W.H.; Dyszlewski, A.D. Tetrahedron Lett. 1987, 28, 3193.

6. Lin, P.; Whitham, G.H.; J. Chem. Soc. Chem. Commun. 1983, 1102.

7. Kocienski, P. J. Chem. Soc. Perkin Trans. 1 1983, 945.

8. Ogura, K.; Iihama, T.; Kiuchi, S.; Kajiki, T.; Koshikawa, O.; Takahasi, K.; Iida, H. J. Org. Chem. 1986, 51, 700.

9. Baechler, R.D.; Bentley, P.; Deuring, L.; Fisk, S. Tetrahedron Lett. 1982, 23, 2269.

10. Johnson, F. Chem. Rev. 1968, 68, 375 and references therein.

11. Allinger, N.L.; Sprague, J.T. J. Am. Chem. Soc. 1972, 94, 5734.

12. a. Cristol, S.J.; Kellman, R. J. Org. Chem. 1971, 36 1866; b. Alden, C.K.; Davies, D.I. J. Chem. Soc. C. 1968, 709; c. Belikova, N.A.; Plate, A.F.; Tabrina, G.M.; Sterin, Kh.E.; Lukashina, V.M.; Pakhomov, V.P.; Berezkin, V.G. Russ. J. Org. Chem. 1965, 498.

13. It is well known that when methylene cyclohexane is substituted with bulkier groups at the C-2 position in the ring, it prefers axial orientation due to the 1,3-allylic strain. For discussion on the latter see reference 10, and Hoffmann, R. Chem. Rev. 1989, 89, 1841.

14. a. Magnus, P.D. Tetrahedron 1977, 33, 2019. b. Moriyana, T.; Mandai, T.; Kawada, M.; Otera, J.; Trost, B.M. J. Org. Chem. 1986, 51, 3896. c. Inomata, K.; Yamamoto, T.; Kotake, H. Chem. Lett. 1981, 1357.

15. Dodd, D.; Johnson, M.D. J. Organometal. Chem. 1973, 52, 1.

16. a. Wheelar, O.H.; Lerner, I. J. Am. Chem. Soc. 1956, 78, 63; b. Arnold, R.T.; Lee, W.W. J. Am. Chem. Soc. 1953, 75, 5396.

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