Homolytic Displacement at Carbon. Part 3.[1–3] First Example of α-Attack on the Allenyl- and Prop-2-ynyl-cobaloximes

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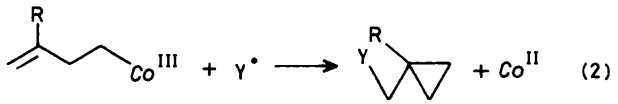
Allenylcobaloxime reacts with substituted benzenesulphonyl chlorides in an inert atmosphere under irradiation with tungsten lamps to give good yields of allenyl sulphones. However, the same reactions carried out in Srinivasan's photoreactor using a 400 W medium-pressure mercury lamp or under thermal conditions give exclusively prop-2-ynyl sulphones, by regiospecific rearrangement, in good yields. The corresponding reactions of (3,3-disubstituted allenyl) cobaloximes afford 1,1-disubstituted prop-2-ynyl sulphones irrespective of the conditions used. Similarly, prop-2-ynyl sulphones are formed exclusively in the reactions of prop-2-ynylcobaloxime with organosulphonyl chlorides under thermal and photochemical conditions. The reactions are believed to take place through a chain mechanism in which cobaloxime(II), present adventitiously or formed by partial homolysis of the substrate cobaloxime, abstracts a chlorine atom from the organosulphonyl chloride to give the organosulphonyl radical $R\dot{S}O_2$. Depending upon the reaction conditions and the nature of cobaloxime, $R\dot{S}O_2$ attacks the α- or the γ-carbon atom of the axial organic group of the cobaloxime, thereby displacing cobaloxime(II) and giving the observed organic product.

A number of papers have described a series of novel displacement reactions between a free radical precursor and a diamagnetic σ-bonded organometallic complex in which the key step is the homolytic displacement of a paramagnetic metal complex by attack of a *C*-, *S*-, or *N*-centred electrophilic radical on the organic ligands of the organometallic complex [reactions (1)—(5)].[1–13]


(1)


(2)

$$R_2C{=}C{=}CH{-}Co^{III} + {}^{\bullet}CCl_3 \longrightarrow CCl_3CR_2C{\equiv}CH + Co^{II} \quad (3)$$

$$PhC{\equiv}C{-}CH_2Co^{III} + {}^{\bullet}CH(CO_2Et)_2 \longrightarrow (CO_2Et)_2CH{-}CPh{=}C{=}CH_2 + Co^{II} \quad (4)$$

$$PhCH_2Co^{III} + Y^{\bullet} \longrightarrow PhCH_2Y + Co^{II} \quad (5)$$

Co = [Co(dmgH)$_2$py]; Y = CCl_3, CBr_3, CCl_2CN, SPh, SO_2R, $ArSO_2NMe$, *etc.*; dmgH = dimethylglyoximate(1−)

Each of the reactions (1)—(5) forms part of a chain process, some times of rather short length, in which the displaced inorganic complex, [Co^{II}(dmgH)$_2$py], is instrumental in the production of an organic radical (*e.g.* $^{\bullet}CCl_3$, $^{\bullet}SO_2R$, *etc.*) from the diamagnetic precursor (*e.g.* $BrCCl_3$, RSO_2Cl, *etc.*) [reactions (6) and (7)].

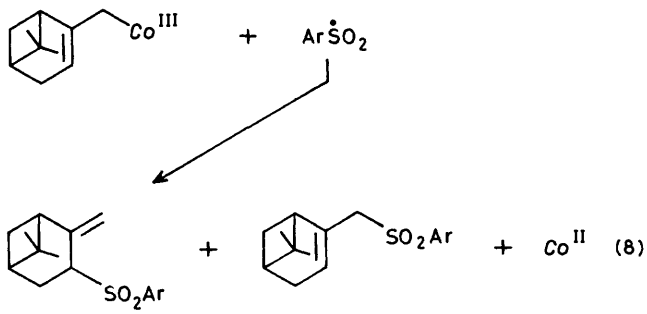
$$M^{\bullet} + XY \longrightarrow MX + Y^{\bullet} \quad (6)$$

$$Y^{\bullet} + RM \longrightarrow RY + M^{\bullet} \quad (7)$$

RM = $RCo^{III}(dmgH)_2py$

The novelty of the process lay particularly in reaction (7), which for various kinds of organic ligand R (allyl, allenyl, prop-2-ynyl, butenyl, hexenyl, benzyl, *etc.*), represented the first example of S_H2' displacement of a transition metal from carbon by attack at the unsaturated carbon centre† and the first example of S_H2 displacement at a saturated carbon centre in solution.‡ This subject is important in view of the very few examples of S_H2 reactions at a carbon centre and their preparative value in organic chemistry.

In reactions (1)—(4), the organic products are formed by regiospecific attack of Y$^{\bullet}$ on the terminal carbon of the axial organic group of the organometallic complex. Exceptions to terminal attack are rare; however, this has been observed with a sterically hindered allylcobaloxime[16] [reaction (8)].


(8)

We report here the first experimental observation that allenyl- and prop-2-ynyl-cobaloximes undergo α attack by an organosulphonyl radical.

† Hegedus and Miller[14] report a reaction R + allyl-NiBr ⟶ R-allyl + NiBr, which might be a homolytic displacement at carbon, but they also consider and cannot rule out an alternative process involving attack of R on nickel followed by a reductive elimination of the organic product.

‡ Jackson[15a] has observed a homolytic displacement at saturated carbon by CF_3 radicals in the gas phase. It seems likely that ring opening of some strained cyclopropane rings by halogens involves attack of halogen atom at a ring carbon atom.[15b]

Results

The reaction between allenylcobaloxime (**1**) and toluene-*p*-sulphonyl chloride (**A4**) in 3:5 molar ratio in dichloromethane containing a few drops of pyridine at 10 °C under anaerobic and photolytic conditions (irradiation with two 200 W tungsten lamps through all-glass apparatus; method P1) is subject to an induction time, the length of which depends upon the conditions and the purity of the substrate cobaloxime. The rate of reaction is lowered or increased by the addition of a catalytic amount of galvinoxyl or dibenzoyl perioxide, respectively. *p*-Tolyl allenyl sulphone (**8**) is the sole organic product, isolated in 53% yield. Careful monitoring of the reaction by checking product distribution every half hour indicates the formation of *p*-tolyl allenyl sulphone from the very beginning, and points further to the fact that the sulphone does not isomerise at any stage even when toluene-*p*-sulphonyl chloride and cobaloxime(II) are present in solution. Similar reactions with *o*-nitro-, *p*-fluoro-, *p*-chloro-, *p*-bromo-, and 2,4,5-trichloro-benzenesulphonyl chlorides, (**A3**) and (**A6**—**9**), respectively, give the corresponding allenyl sulphones (**7**) and (**9**)—(**12**) in 45—76% yield. In addition, a small amount ($\leqslant 5\%$) of another isomer, the prop-2-ynyl sulphone, (**14**) or (**15**), is also formed in the reaction of (**1**) with (**A4**) or (**A7**). However, the reactions of allenylcobaloxime (**1**) with *p*-methyl-, *p*-chloro-, and *p*-bromo-benzenesulphonyl chloride, (**A4**), (**A7**), and (**A8**), under anaerobic and thermal conditions (refluxing dichloromethane; method T1) or under photochemical conditions (Srinivasan's photoreactor with a 400 W mercury lamp; method P2) give solely the prop-2-ynyl sulphones (**14**)—(**16**), the yields of which are higher under photochemical than under thermal conditions. In sharp contrast, benzenesulphonyl chloride (**A2**) forms a 1:1 mixture of allenyl (**6**) and prop-2-ynyl (**6′**) sulphones under all three conditions (P1, T1, and P2). The case of methanesulphonyl chloride (**A1**) is similar; the prop-2-ynyl sulphone (**13**) is the exclusive product from (**1**) under all conditions.

The corresponding reactions of the (3,3-disubstituted allenyl)-cobaloximes (**2**)—(**4**) with (**A1**) and (**A4**—**9**) give exclusively the products of regiospecific rearrangement, the prop-2-ynyl sulphones (**17**)—(**31**) under all three reaction conditions (T1, P1, and P2). Prop-2-ynylcobaloxime (**5**), on the other hand, under all three conditions reacts with (**A1**), (**A4**), and (**A7**—**9**) to give the corresponding prop-2-ynyl sulphones (**13**)—(**16**) and (**32**). The characteristics of all the sulphones are given in Schemes 1—3 and Tables 1 and 2.

$$\underset{(1)}{CH_2{=}C{=}CHCo^{III}(dmgH)_2py} + RSO_2Cl \xrightarrow[\text{method P1}]{h\nu} CH_2{=}C{=}CHSO_2R + ClCo^{III}(dmgH)_2py$$

(**A2**) R = Ph	(**6**) R = Ph[a]
(**A3**) R = 2-$NO_2C_6H_4$	(**7**) R = 2-$NO_2C_6H_4$
(**A4**) R = 4-MeC_6H_4	(**8**) R = 4-MeC_6H_4[b]
(**A6**) R = 4-FC_6H_4	(**9**) R = 4-FC_6H_4
(**A7**) R = 4-ClC_6H_4	(**10**) R = 4-ClC_6H_4[b]
(**A8**) R = 4-BrC_6H_4	(**11**) R = 4-BrC_6H_4
(**A9**) R = 2,4,5-$Cl_3C_6H_2$	(**12**) R = 2,4,5-$Cl_3C_6H_2$

Scheme 1.

[a] An equal amount of prop-2-ynyl sulphone $CH{\equiv}C{-}CH_2SO_2Ph$ (**6′**) is also formed. [b] A small amount ($\leqslant 5\%$) of the other isomer $CH{\equiv}C{-}CH_2SO_2R$ [(**14**) R = 4-MeC_6H_4 or (**15**) R = 4-ClC_6H_4] is also formed.

$$R^1R^2C{=}C{=}CHCo^{III}(dmgH)_2py + RSO_2Cl \xrightarrow[\text{method T1/P1/P2}]{h\nu, \text{ or heat}} CH{\equiv}C{-}CR^1R^2{-}SO_2R + ClCo^{III}(dmgH)_2py$$

(**1**) $R^1 = R^2 = H$	(**A1**) R = Me	(**13**) $R^1 = R^2 = H$, R = Me
	(**A4**)	(**14**) $R^1 = R^2 = H$, R = 4-MeC_6H_4[a]
	(**A7**)	(**15**) $R^1 = R^2 = H$, R = 4-ClC_6H_4[a]
	(**A8**)	(**16**) $R^1 = R^2 = H$, R = 4-BrC_6H_4[a]
(**2**) $R^1 = R^2 = Me$	(**A4**)	(**17**) $R^1 = R^2 = Me$, R = 4-MeC_6H_4
	(**A7**)	(**18**) $R^1 = R^2 = Me$, R = 4-ClC_6H_4
	(**A8**)	(**19**) $R^1 = R^2 = Me$, R = 4-BrC_6H_4
	(**A9**)	(**20**) $R^1 = R^2 = Me$, R = 2,4,5-$Cl_3C_6H_2$
(**3**) R^1 = Me, R^2 = Et	(**A1**)	(**21**) R^1 = Me, R^2 = Et, R = Me
	(**A4**)	(**22**) R^1 = Me, R^2 = Et, R = 4-MeC_6H_4
	(**A5**) R = 4-$MeOC_6H_4$	(**23**) R^1 = Me, R^2 = Et, R = 4-$MeOC_6H_4$
	(**A6**)	(**24**) R^1 = Me, R^2 = Et, R = 4-FC_6H_4
	(**A7**)	(**25**) R^1 = Me, R^2 = Et, R = 4-ClC_6H_4
	(**A8**)	(**26**) R^1 = Me, R^2 = Et, R = 4-BrC_6H_4
	(**A9**)	(**27**) R^1 = Me, R^2 = Et, R = 2,4,5-$Cl_3C_5H_2$
(**4**) $R^1 R^2 = [CH_2]_5$	(**A4**)	(**28**) $R^1R^2 = [CH_2]_5$, R = 4-MeC_6H_4
	(**A7**)	(**29**) $R^1R^2 = [CH_2]_5$, R = 4-ClC_6H_4
	(**A8**)	(**30**) $R^1R^2 = [CH_2]_5$, R = 4-BrC_6H_4
	(**A9**)	(**31**) $R^1R^2 = [CH_2]_5$, R = 2,4,5-$Cl_3C_6H_2$

Scheme 2.

[a] Obtained only under T1 and P2 conditions.

$$\underset{(5)}{CH{\equiv}C{-}CH_2Co^{III}(dmgH)_2py} + RSO_2Cl \xrightarrow[\text{method T1/P1 or P2}]{h\nu \text{ or heat}} CH{\equiv}C{-}CH_2SO_2R + ClCo^{III}(dmgH)_2py$$

(A1)	(13)
(A4)	(14)
(A7)	(15)
(A8)	(16)
(A9)	(32) R = 2,4,5-$Cl_3C_6H_2$

Scheme 3.

Discussion

All the reactions described in this paper are free radical in nature. Although the evidence is indirect, it is certain that the free radicals abound under all the conditions described. Since cleavage of the Co–C bond is a key feature of the reactions of these substrates, it is important to examine the tendency of the organocobaloximes to undergo unimolecular homolysis. It is well established that thermolysis and photolysis of the Co–C bond in organocobaloximes take place very readily even on irradiation at wavelengths greater than 360 nm.[17] This is consistent with the low Co–C bond energy, 17—25 kcal mol^{-1} in such substrates.[18] Tungsten lamps and glass apparatus are, therefore, adequate for preparative photolysis experiments. The order of thermal stability of organocobaloximes in solution, which reflects the stability of the Co–C bond, is, 1-methylvinyl < allyl < benzyl < t-alkyl < s-alkyl < n-alkyl. Thus the least stable complexes dissociate at or below ambient temperature[19] and secondary alkyl complexes show some evidence of homolysis above 80 °C, whereas primary alkylcobaloximes show little decomposition below 100 °C. Furthermore, cobaloxime(II) is capable of reacting rapidly with the halogen atom of an organosulphonyl halide; *e.g.* preformed cobaloxime(II) reacts effectively and rapidly on a preparative scale in non-aqueous solvents with tetrachloromethane and trichloromethanesulphonyl chloride to form a 1:1 mixture of chlorocobaloxime and the unstable trichloromethylcobaloxime.[20] In addition, cobaloxime(II) has also been shown to be a good leaving group in many homolytic displacement reactions. In view of the results of many known reactions of *C*-, *S*-, or *N*-centred radicals with allyl-, butenyl-, pentenyl-, allenyl-, and benzylcobaloximes,[1–13,21–23] it seems that allenylcobaloxime may react in a number of possible ways with organosulphonyl halides, *e.g.* (i) free radical addition at the double bond followed by Co–C bond cleavage; (ii) cleavage of the Co–C bond and subsequent reactions of allenyl radical leading to a variety of products; or (iii) S_H2' or S_H2 reactions at a carbon centre displacing cobaloxime(II).

From the regiospecific nature of the products and the influence of galvinoxyl and dibenzoyl peroxide, it seems that reaction (iii) is the most prominent in our studies. We believe that the mechanism is similar to that proposed by us for the reaction of allylcobaloxime with *p*-substituted benzenesulphonyl chlorides.[1] The key feature is attack of the sulphonyl radical, formed by capture of a chlorine atom from the organosulphonyl chloride by cobaloxame(II), at the carbon centre of the allenylcobaloxime.

Path A

$$Co^{II}(dmgH)_2py + RSO_2Cl \longrightarrow R\dot{S}O_2 + ClCo^{III}(dmgH)_2py \quad (9)$$

$$R\dot{S}O_2 + CH_2{=}C{=}CHCo^{III}(dmgH)_2py \longrightarrow CH_2{=}C{=}CHSO_2R + Co^{II}(dmgH)_2py \quad (10)$$

Path B

$$Co^{II}(dmgH)_2py + RSO_2Cl \longrightarrow R\dot{S}O_2 + ClCo^{III}(dmgH)_2py \quad (9)$$

$$R\dot{S}O_2 + CH_2{=}C{=}CHCo^{III}(dmgH)_2py \longrightarrow RSO_2{-}CH_2{-}C{\equiv}CH + Co^{II}(dmgH)_2py \quad (11)$$

The products $CH_2{=}C{=}CHSO_2R$ and $CH{\equiv}C{-}CH_2SO_2R$ may arise by two independent routes involving propagation steps (9) and (10) (α-attack, path A) and (9) and (11) (γ-attack, path B). The most unusual features of these reactions is the exclusive formation of products by substitution at the α-carbon of the axial organic group. Furthermore, the results indicate that the attack of the $R\dot{S}O_2$ radical on the α- or γ-carbon atom of the allenylcobaloxime depends upon various factors including (i) the nature of the radical used, (ii) the nature of the substituent in the parent cobaloxime, and (iii) the reaction conditions.

It has been observed in several reactions of allyl- and butenylcobaloximes with *C*-, *S*-, or *N*-centred radicals that attack of the free radical occurs exclusively at the olefinic carbon atom of the axial organic group, and kinetically controlled products of regiospecific rearrangement are obtained.[1–13,21–23] It is not that the attacking radical always aims at the terminal carbon centre; for example, (*a*) displacement at the α-carbon atom of an alkyl chain is found to be a dominant process under appropriate conditions if the attack is intramolecular and capable of forming a five-membered cyclic sulphone,[13,24] (*b*) attack at the α-carbon atom is favoured when the terminal carbon atom is sufficiently sterically hindered, as in α-pinenylcobaloxime.[6] Therefore, the regiospecificity observed in the case of allylcobaloximes with various radical precursors is merely fortuitous and the extent of regiospecificity depends not only on the nature of the organocobaloximes but also on the nature of the attacking radical; for example, $^{\bullet}CCl_3$ reacts substantially regiospecifically with cyclopent-1-enylmethyl- and cyclohex-1-enylmethyl-cobaloximes to give exocyclic methylene products, whereas α-cyanomethyl radical seems not to react regiospecifically even with unhindered allylcobaloxime.[25]

In all the reactions already discussed, kinetically controlled products seem to be formed always. However, in the present studies since the α-carbon atom bonded to cobalt in allenylcobaloxime is more nucleophilic than the γ-carbon, and the γ-carbon atom is more nucleophilic than the α-carbon in (3,3-disubstituted allenyl)cobaloxime, it would be expected that the electrophilic organosulphonyl radical $R\dot{S}O_2$ would preferentially attack the α-carbon atom in allenylcobaloxime and the γ-carbon in the disubstituted allenylcobaloxime, especially if kinetic factors do not play a significant role in controlling the selectivity. Although this is a very simplisitic view, it is difficult to separate kinetic and the thermodynamic factors in reactions of allenylcobaloximes. Consideration of factors like thermodynamic stability of sulphones, isomerisation of acetylenic sulphones to allenic sulphones (and *vice versa*), and coupling reactions is, therefore, important. The thermodynamic stability of the sulphones[26] which falls in the order $RC{\equiv}C{-}CH_2SO_2R > RCH{=}C{=}CHSO_2R > CH{\equiv}C{-}CH_2SO_2R$ cannot be taken as direct evidence in support of the present results because if the allenyl sulphone is thermodynamically more stable than the prop-2-ynyl sulphone, then in the reaction of prop-2-ynylcobaloximes with $R\dot{S}O_2$, the allenyl sulphone should have been formed (by γ-attack). As isomerisation of acetylenic to allenic sulphones (and *vice versa*) under thermal, photochemical,

Table 1. Organic products from the reactions of allenyl- and prop-2-ynyl-cobaloximes with organosulphonyl chlorides (RSO_2Cl)

Cobaloxime	RSO_2Cl[a]	Product	Conditions[b]	Isolated[c] yield (%)	M.p. (°C)	Found (Calc.) (%) C	H
Allenyl (**1**)	(**A1**)	$CH{\equiv}CCH_2SO_2Me$ (**13**)	T1/P1/P2	64[d]	(Oil)	40.65 (40.65)	5.1 (5.1)
	(**A2**)	$CH_2{=}C{=}CHSO_2Ph$ (**6**) + $CH{\equiv}CCH_2SO_2Ph$ (**6′**)	T1/P1/P2	73[d] (1:1)	65—67	59.9 (60.0)	4.4 (4.5)
					e	59.9 (60.0)	4.45 (4.45)
	(**A3**)	$CH_2{=}C{=}CHSO_2C_6H_4NO_2$-2 (**7**)	P1	45	(Oil)	47.9 (48.0)	3.1 (3.2)
	(**A4**)	$CH_2{=}C{=}CHSO_2C_6H_4Me$-4 (**8**)	P1	53	71	61.8 (61.9)	5.15 (5.2)
	(**A4**)	$CH{\equiv}CCH_2SO_2C_6H_4Me$-4 (**14**)	T1/P2	68	*e*	61.8 (61.8)	5.2 (5.2)
	(**A6**)	$CH_2{=}C{=}CHSO_2C_6H_4F$-4 (**9**)	P1	51	(Oil)	54.5 (54.4)	3.5 (3.6)
	(**A7**)	$CH_2{=}C{=}CHSO_2C_6H_4Cl$-4 (**10**)	P1	64	(Oil)	50.3 (50.4)	3.3 (3.3)
	(**A7**)	$CH{\equiv}CCH_2SO_2C_6H_4Cl$-4 (**15**)	T1/P2	70	*e*	50.3 (50.4)	3.3 (3.3)
	(**A8**)	$CH_2{=}C{=}CHSO_2C_6H_4Br$-4 (**11**)	P1	66	62	41.7 (41.7)	2.7 (2.7)
	(**A8**)	$CH{\equiv}CCH_2SO_2C_6H_4Br$-4 (**16**)	T1/P2	72	39—41	41.7 (41.7)	2.7 (2.7)
	(**A9**)	$CH_2{=}C{=}CHSO_2C_6H_2Cl_3$-2,4,5 (**12**)	P1	76	*e*	38.0 (38.1)	1.7 (1.8)
3-Methylbuta-1,2-dienyl (**2**)	(**A4**)	$CH{\equiv}CCMe_2SO_2C_6H_4Me$-4 (**17**)	T1/P1/P2	71	94	64.8 (64.8)	6.3 (6.35)
	(**A7**)	$CH{\equiv}CCMe_2SO_2C_6H_4Cl$-4 (**18**)	T1/P1/P2	68	65	54.4 (54.4)	4.6 (4.6)
	(**A8**)	$CH{\equiv}CCMe_2SO_2C_6H_4Br$-4 (**19**)	T1/P1/P2	62[d]	97	45.9 (46.0)	3.8 (3.9)
	(**A9**)	$CH{\equiv}CCMe_2SO_2C_6H_2Cl_3$-2,4,5 (**20**)	T1/P1/P2	74	101	42.4 (42.4)	2.9 (2.95)
3-Methylpenta-1,2-dienyl (**3**)	(**A1**)	$CH{\equiv}CCMeEtSO_2Me$ (**21**)	T1/P1/P2	52[d]	(Oil)	52.45 (52.4)	7.5 (7.55)
	(**A4**)	$CH{\equiv}CCMeEtSO_2C_6H_4Me$-4 (**22**)	T1/P1/P2	63	82	66.3 (66.4)	6.4 (6.4)
	(**A5**)	$CH{\equiv}CCMeEtSO_2C_6H_4OMe$-4 (**23**)	T1/P1/P2	60	76—77	62.1 (62.15)	6.0 (6.0)
	(**A6**)	$CH{\equiv}CCMeEtSO_2C_6H_4F$-4 (**24**)	T1/P1/P2	55[d]	59—61	59.9 (60.0)	5.4 (5.45)
	(**A7**)	$CH{\equiv}CCMeEtSO_2C_6H_4Cl$-4 (**25**)	T1/P1/P2	72	61	56.1 (56.1)	5.1 (5.1)
	(**A8**)	$CH{\equiv}CCMeEtSO_2C_6H_4Br$-4 (**26**)	T1/P1/P2	68	78	47.8 (47.85)	4.3 (4.35)
	(**A9**)	$CH{\equiv}CCMeEtSO_2C_6H_2Cl_3$-2,4,5 (**64**)	T1/P1/P2	64[d]	80—81	44.2 (44.3)	3.4 (3.4)
Cyclohexylidenevinyl (**4**)	(**A4**)	$CH{\equiv}CC([CH_2]_5)SO_2C_6H_4Me$-4 (**28**)	T1/P1/P2	72	126	68.6 (68.7)	6.9 (6.9)
	(**A7**)	$CH{\equiv}CC([CH_2]_5)SO_2C_6H_4Cl$-4 (**29**)	T1/P1/P2	75	174	59.5 (59.5)	5.35 (5.35)
	(**A8**)	$CH{\equiv}CC([CH_2]_5)SO_2C_6H_4Br$-4 (**30**)	T1/P1/P2	72	193	51.4 (51.4)	4.6 (4.6)
	(**A9**)	$CH{\equiv}CC([CH_2]_5)SO_2C_6H_2Cl_3$-2,4,5 (**31**)	T1/P1/P2	76	138	47.8 (47.85)	3.7 (3.7)
Prop-2-ynyl (**5**)	(**A1**)	$CH{\equiv}CCH_2SO_2Me$ (**13**)	T1/P1/P2	78	(Oil)	40.65 (40.7)	5.1 (5.1)
	(**A4**)	$CH{\equiv}CCH_2SO_2C_6H_4Me$-4 (**14**)	T1/P1/P2	73	*e*	61.8 (61.8)	5.15 (5.2)
	(**A7**)	$CH{\equiv}CCH_2SO_2C_6H_4Cl$-4 (**15**)	P1/P2	65[d]	*e*	50.3 (50.4)	3.2 (3.3)
	(**A8**)	$CH{\equiv}CCH_2SO_2C_6H_4Br$-4 (**16**)	P2	72	40—41	41.7 (41.7)	2.65 (2.7)
	(**A9**)	$CH{\equiv}CCH_2SO_2C_6H_2Cl_3$-2,4,5 (**32**)	P2	81	44—45	38.1 (38.1)	1.7 (1.8)

[a] For (**A1**)—(**A9**) see Schemes. [b] For details refer to Experimental section. [c] In cases where the reactions are performed under more than one set of conditions, the yields reported are for P2, unless otherwise stated. [d] For P1. [e] M.p. < 30 °C.

Table 2. Spectral characteristics[a] of allenyl sulphones, CH_2=C=CHSO$_2$R (**6**)—(**12**), prop-2-ynyl sulphones (CH≡CCH$_2$SO$_2$R) (**13**)—(**16**), (**6′**), and (**32**), and 1,1-disubstituted prop-2-ynyl sulphones CH≡CC(R^{1}R^2)SO$_2$R (**17**)—(**31**)

	δ_H(CDCl$_3$) [J/Hz][b]							
Product	1-H	1-R	3-H	Aromatic	Other	m/z[c]	$\lambda_{max.}$/nm (MeOH)	$\nu_{max.}$/cm^{-1}[d]
(**6**)	6.20 (t)		5.37 (d)	7.3—7.9 (m)		180, 77	237, 264, 275	1 150, 1 330, 1 920, 1 965
(**7**)	6.70 (t)		5.52 (d)	7.71 (br, s), 8.09 (m)		225, 122	235, 265	1 145, 1 340, 1 920, 1 970
(**8**)	6.20 (t)		5.40 (d)	7.30, 7.74 [8]	2.46 (Me)	194, 91	232, 262, 274	1 160, 1 335, 1 930, 1 970
(**9**)	6.18 (t)		5.38 (d)	7.16 (m), 7.84 (m)		198, 95	230, 260, 271	1 155, 1 325, 1 930, 1 965
(**10**)	6.20 (t)		5.42 (d)	7.46, 7.78 [9]		214, 111	233, 263, 275	1 150, 1 325, 1 930, 1 970
(**11**)	6.21 (t)		5.40 (d)	7.70 (dd) [6]		258, 155, 260, 157	240, 279	1 150, 1 325, 1 930, 1 970
(**12**)	6.38 (t)		5.50 (d)	7.60 (s), 8.16 (s)		282, 179	238, 257, 294	1 150, 1 335, 1 920, 1 965
(**13**)	4.28 (dd)		1.40 (dd)		3.00 (s, Me)	118	219, 241, 275	1 160, 1 330, 3 300
(**14**)	4.02 (dd)		1.30 (dd)	7.37, 7.72 [8]	2.41 (s, Me)	194	224, 260, 272	1 160, 1 330, 3 320
(**15**)	4.10 (dd)		1.32 (dd)	7.40, 7.74 [7]		214	226, 263, 272	1 160, 1 335, 3 300
(**16**)	4.11 (dd)		1.31 (dd)	7.66 (dd) [5]		258, 260	233, 251, 278	1 160, 1 330, 3 300
(**17**)		1.60 (s, Me)	2.50 (s)	7.29, 7.80 [8]	2.46 (Me)	222	225, 263	1 135, 1 165, 1 305, 3 260
(**18**)		1.58 (s, Me)	2.47 (s)	7.48, 7.88 [8]		242	228, 270	1 130, 1 160, 1 305, 3 260
(**19**)		1.54 (s, Me)	2.40 (s)	7.64 (dd)		286, 288	233, 265, 274	1 125, 1 155, 1 300, 3 260
(**20**)		1.66 (s, Me)	2.49 (s)	7.60 (s), 8.14 (s)		310	215, 237, 292	1 165 (br, s), 1 330, 3 285
(**21**)		1.16 (m) and 1.7—2.1 (m) (Et), 1.61 (s, Me)	2.57 (s)		3.00 (Me)	160	237, 255, 270	1 160, 1 300, 3 240
(**22**)		1.06 (m) and 1.7—2.1 (m) (Et), 1.53 (s, Me)	2.47 (s)	7.65, 8.20 [8]	2.40 (Me)	236	227, 262, 276	1 160, 1 300, 3 250
(**23**)		1.08 (m) and 1.7—2.1 (m) (Et), 1.52 (s, Me)	2.44 (s)	6.94, 7.82 [8.5]	3.84 (OMe)	252	235, 249 268	1 165, 1 305, 3 240
(**24**)		1.2 (m) and 1.8—2.1 (m) (Et), 1.57 (s, Me)	2.48 (s)	7.22 (m), 7.96 (m)		240	237, 251 272	1 160, 1 300, 3 250
(**25**)		1.14 (m) and 1.8—2.1 (m) (Et), 1.54 (s, Me)	2.48 (s)	7.48, 7.87 [7.5]		256	229, 260	1 160, 1 310, 3 260
(**26**)		1.1 (m) and 1.8—2.1 (m) (Et), 1.52 (s, Me)	2.48 (s)	7.60. 7.80 [7]		300, 302	236, 266, 276	1 155, 1 310, 3 270
(**27**)		1.15 (m) and 1.9—2.1 (m) (Et), 1.65 (s, Me)	2.58 (s)	7.62 (s), 8.20 (s)		324	236, 287, 295	1 155 (br, s), 1 335, 3 280
(**28**)		1.5—2.1 (m, [CH$_2$]$_5$)	2.50 (s)	7.28, 8.00 [8]	2.44 (s, Me)	262	229, 262,	1 150, 1 305, 3 250
(**29**)		1.6—2.0 (m, [CH$_2$]$_5$)	2.51 (s)	7.45, 7.83 [7.5]		282	230	1 150, 1 310, 3 260
(**30**)		1.4—2.2 (m, [CH$_2$]$_5$)	2.66 (s)	7.64, 7.80 [6]		326, 328	237	1 140, 1 310, 3 260
(**31**)		1.5—2.2 (m, [CH$_2$]$_5$)	2.58 (s)	7.60 (s), 8.18 (s)		350	221, 234, 288	1 155 (br, s), 1 330, 3 280

[a] Spectral characteristics of (**6′**): δ 3.93 (1 H, dd), 1.26 (3 H, dd), 7.2—7.85 (aromatic, m); m/z 180 (M^+); $\lambda_{max.}$ 231, 264, and 274 nm; $\nu_{max.}$ 1 155, 1 330, and 3 300 cm^{-1}. Spectra characteristics of (**32**): δ 4.12 (1 H, dd), 1.35 (3 H, dd), 7.48 (s), and 7.9 (s) (aromatic); m/z 282 (M^+); $\lambda_{max.}$ 221, 255, and 294 nm; $\nu_{max.}$ 1 150, 1 325, and 3 280 cm^{-1}. [b] J_{13} = 6 Hz in most cases; however, for (**6**), (**15**), and (**32**), J_{13} 5, 4, and 5 Hz, respectively. [c] A single value refers to M^+, while, two values refer to M^+ and R, respectively. [d] $\nu_{sym.}$ SO$_2$ 1 150—1 160 cm^{-1} for (**6**)—(**16**), (**6′**), and (**32**); 1 125—1 165 cm^{-1} for (**17**)—(**31**); $\nu_{asym.}$ SO$_2$ 1 325—1 340 cm^{-1} for (**6**)—(**12**); 1 325—1 335 cm^{-1} for (**13**)—(**16**), (**6′**), and (**32**); 1 300—1 330 cm^{-1} for (**17**)—(**31**). ν(–C=C=C–) 1 920—1 970 cm^{-1} for (**6**)—(**12**); ν(HC≡C–) 3 280—3 320 cm^{-1} for (**13**)—(**16**), (**6′**), and (**32**); 3 240—3 285 cm^{-1} for (**17**)—(**31**).

or base-catalysed conditions has been reported,[27,28] it is the allenyl sulphones in the present study may have arisen by such a process. This possibility, however, has been ruled out by our observation that no such isomerisation takes place in independent experiments on allenyl and prop-2-ynyl sulphones under identical conditions. Furthermore, allenylcobaloxime does not isomerise to prop-2-ynylcobaloxime in the absence of sulphonyl radicals. Since the reactions of allenyl- and prop-2-ynylcobaloximes [(**1**) and (**5**)] with organosulphonyl halides give exclusively allenyl and prop-2-ynyl sulphones, we propose

that the allenyl sulphones (**6**)—(**12**) do not arise by any coupling process of the type (12). This is justified, because if the coupling

$$R\dot{S}O_2 + CH_2{=}C{=}\dot{C}H \longrightarrow CH_2{=}C{=}CHSO_2R \quad (12)$$

were taking place at all, one would expect the formation of a mixture of allenyl and prop-2-ynyl suphones in each reaction, since the allenyl and prop-2-ynyl radicals have generally been considered to exist in mutually resonating forms.[29] The absence of such a mixture suggests that at any given time the concentration of allenyl or prop-2-ynyl radicals is very small, and hence no coupling occurs.

It is thus clear that the formation of allenyl and prop-2-ynyl sulphones from the corresponding organocobaloximes is due to a novel S_H2 process involving the attack of $R\dot{S}O_2$ at the α-carbon centre of the axial organic group. These reactions are the first examples of such S_H2 α-attack in allenyl- and prop-2-ynylcobaloximes. However, attack of the $R\dot{S}O_2$ radical on the terminal carbon atom of the allenyl group in (**1**) under thermal (T1) or photochemical (P2) conditions is surprising; no obvious explanation appears at this stage. It is possible that the thermal reaction contributes under P2 conditions.* Similarly, the formation of a mixture of acetylenic and allenic sulphones from $Ph\dot{S}O_2$ and only the acetylenic sulphone (**13**) from $Me\dot{S}O_2$ suggests that the electrophilicity of the attacking radical may be an important factor. With this in mind, a study with captodative radicals is in progress in our laboratory.

The simple allenyl sulphones have been reported previously; synthetic methods have included oxidation of allenic sulphides[30] or sulphoxides,[31] base-catalysed isomerisation of prop-2-ynyl sulphones,[32] and thermal [2,3]sigmatropic rearrangement of prop-2-ynyl arenesulphinates.[33] In view of the ready formation of the cobaloximes from the readily available and inexpensive prop-2-ynyl halides, the present reactions provide the most valuable and simple synthetic approach to allenyl and prop-2-ynyl sulphones.

Experimental

Material and Instrumentation.—Methanesulphonyl chloride, benzenesulphonyl chloride, *o*-nitro-, *p*-methyl-, *p*-fluoro-, *p*-chloro-, *p*-bromo-, and 2,4,5-trichloro-benzenesulphonyl chlorides, prop-2-yn-1-ol, 2-methylbut-3-yn-2-ol, 3-methylpent-1-yn-3-ol, and 1-ethynylcyclohexanol were all commercial materials and were recrystallised or distilled before use. M.p.s were determined with a Fisher-Johns apparatus. I.r. spectra were recorded with a Perkin-Elmer 377 and 580 grating spectrophotometers. Electronic spectra were recorded with Cary-17D and Shimadzu UV-190 double-beam spectrophotometers. ^{1}H N.m.r. spectra were measured at 80 MHz with a Bruker WP-80, at 90 MHz with a Varian EM-390, and at 100 MHz with a Varian HA-100 instrument. Mass spectra were measured at the Regional Sophisticated Instrumentation Centres at Lucknow and Madras with a VG Micromass 7070F mass spectrophotometer. Elemental analyses were carried out at the Central Microanalytical Laboratory, I.I.T., Kanpur and at R.S.I.C. Lucknow.

Synthesis of Cobaloximes.—All the cobaloximes were synthesized by the literature procedure from bis(dimethylglyoximate)-pyridinecobalt(I) and organic halides.[34] Cobaloxime(I) was generated *in situ* by anaerobic alkaline disproportionation of cobaloxime(II) in methanol as described by Schrauzer[35] or by the reduction of chlorocobaloxime with $NaBH_4$. Prop-2-yn-1-ol was converted into prop-2-ynyl bromide by treatment with phosphorus tribromide.[36] 3-Chloro-3-methylbut-1-yne, 3-chloro-3-methylpent-1-yne, and 1-chloro-1-ethynylcyclohexane were prepared from the corresponding alcohol by treatment with Cu_2Cl_2 and HCl as described in the literature.[37] All cobaloximes give satisfactory ^{1}H n.m.r. spectra.[34]

Reaction of Cobaloximes with Organosulphonyl Chlorides.—(i) *Photochemical reaction with two* 200 W *tungsten lamps* (*method P1*). The reactions were carried out in a specially designed all-glass apparatus with an external water-cooling system. Pyridine (5 drops), organocobaloxime (2 mmol), and organosulphonyl chloride (2.5—5.0 mmol) were successively added to degassed dichloromethane (50 ml). The solution was irradiated with two 200 W tungsten lamps 5 cm away from the reaction vessel while cold water was circulated through the water jacket. The reaction, which took 3—4 h, was monitored for cobaloxime by t.l.c. on silica gel with ethyl acetate as eluant. After complete reaction, the mixture was concentrated *in vauco* and subjected directly to flash chromatography with dichloromethane–light petroleum (b.p. 40—60 °C) (4:1 v/v) as eluant. The unchanged sulphonyl chloride was eluted first, followed by organic product. Elution with dichloromethane–acetone (1:4) then gave the inorganic product. The organic product was further purified by preparative t.l.c. with dichloromethane–light petroleum (b.p. 60—80 °C) (4:1 v/v) as eluant. The solid product was further recrystallised from light petroleum (b.p. 60—80 °C)–chloroform (4:1 v/v) to give a white solid.

(ii) *Photochemical reaction in Srinivasan's photoreactor with a* 400 W *mercury lamp* (*method P2*). A thoroughly degassed solution of a mixture of organocobaloxime (2 mmol), benzenesulphonyl chloride (3 mmol), and pyridine (5 drops) in dry chloroform (45 ml), placed inside the quartz tubes of the photoreactor, was irradiated with a 400 W mercury lamp† while ice-cold water was circulated through the outer jacket, maintaining the temperature at 25 °C. The reaction took around 2 h. The monitoring and work-up procedure was similar to that for method P1.

(iii) *Thermal reaction* (*method T1*). The reaction method was similar to method P1 except that the mixture of organocobaloxime, organsulphonyl chloride, and pyridine in dichloromethane was heated to reflux on a water-bath under nitrogen. The reaction time was 4—6 h in all cases.

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* This has been pointed out by a referee.

† A 400 W mercury lamp (medium-pressure) emits radiation predominantly at 365—366 nm, with smaller amounts in the u.v. region at 297, 303, 313, and 334 nm, as well as significant amounts in the visible region at 404—408, 436, 546, and 577—579 nm.

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