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Organocobaloxime in organic synthesis: efficient trapping of 5-phenylpent-4-ynyl radical by useful functional groups *

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Abstract

5-Phenylpent-4-ynyl cobaloxime, R(Co^{III}) reacts with the free radical precursors XY [X = CCl_3, CCl_2CN, PhQ, 2,4-$(NO_2)_2C_6H_3$–S, PhSe; Y = Cl, Br, PhQ; Q = S, Se, Te] under thermal or photochemical conditions to give the corresponding organic product RX or RY, depending on the precursor. A non-chain radical mechanism is invoked to account for the product distribution.

Key words: Cobaloxime; Radical

1. Introduction

Studies of transition metal mediated organic synthesis have stimulated much interest in aspects of free radical chemistry [1], as is demonstrated by work on organotin, chromium and titanium reagents. Among the newer reagents, organo-bis(dimethylglyoximato)(pyridine)cobalt(+3) complexes, commonly referred to as organocobaloximes (Scheme 1) have been shown to be excellent precursors for mediation of various free radical transformations [2]. Owing to the very low metal–carbon bond energy (17–26 kcal mol^{-1}) in these complexes, unimolecular homolysis of R–(Co^{III}) can be readily effected [3] by irradiation with visible light which reversibly generates $\dot{R}$ and Co^{II} (Scheme 1).

We became interested in the way in which the organic radical R might best be trapped by a suitable trapping agent. Such trapping could make available a straightforward route to functionalized organic derivatives originating from organocobaloximes R–(Co^{III}). We describe below the efficient trapping of the 5-phenylpent-4-ynyl radical (hereafter denoted by R) by various heteroatom radicals in the reaction of 5-phenyl-4-ynyl cobaloxime (**1**) with various radical trapping agents XY.

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2. Results

The reaction of **1** and CCl_4 (**2a**) (1:2 molar equivalent) in dry dichloromethane at 0–5°C under irradiation with a 500 W sunlamp in inert nitrogen proceeds to completion as indicated by TLC, within 16 h. Chromatographic separation gives 5-phenylpent-4-ynyl chloride (**3**) as the only organic product in 63% isolated yield along with trichloromethylcobaloxime (**4**) as the inorganic product (Table 1).

Similar reaction of **1** with bromotrichloromethane (**2b**) yields the bromide **5**, whereas use of trichloroacetonitrile (**2c**) results in the formation of 5-phenylpent-4-yne (**6**) along with the halide, **3**; the inorganic product in the latter case is cyano(dichloro)methyl cobaloxime (**7**). Reactions of **1** with well-known radical trapping agents, *viz.* diphenyl disulfide (**2d**), diphenyl diselenide (**2e**) and diphenyl ditelluride (**2f**) give the corresponding 5-phenylpent-4-ynyl-sulfide (**8**), -selenide (**10**) and -telluride (**12**) as the sole organic products; the associated inorganic products are PhQCo^{III} $(dmgH)_2Py$ (Q = S, **9**; Se, **11**; Te, **13**). When **1** reacts under the above photolysis conditions with 2,4-dinitrobenzenesulfenyl chloride (**2g**), the sulfide (**14**) is obtained along with chlorocobaloxime (**15**). In sharp contrast, reaction with phenylselenyl bromide (**2h**) affords a mixture of selenides **10** and **26** along with bromocobaloxime (**17**).

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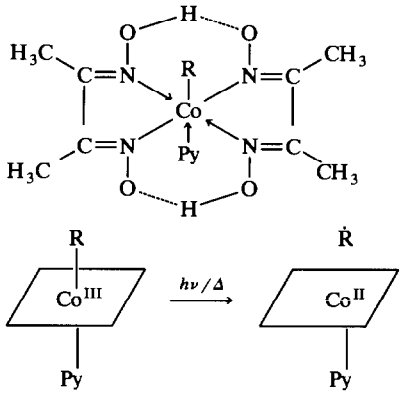

Scheme 1.

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

(1) No rearrangement or decomposition of cobaloxime (**1**) takes place upon photolysis for several days, and **1** is recovered quantitatively.

(2) The reactions mentioned above show a distinct concentration-dependent induction period. This induction period was reduced by addition of 0.01 mol equiv. of dibenzoyl peroxide. On the other hand, addition of 0.01 mol. equiv. of galvinoxyl inhibits the reaction so that the induction period is increased to 6 h.

(3) The reactions show no free-radical chain behaviour. Thus, after the induction period the reaction stops immediately as the light source is turned off, and restarts after a further period of induction when the light source is again turned on. It should be noted that the individual times shown in Table 1 are for reactions under constant illumination and do not include the induction period. Radical promoters such as dibenzoyl peroxide or radical scavengers such as galvinoxyl have no marked effect on the reaction time as defined above.

$$R\text{-}Co^{III} \rightleftharpoons [\dot{R} + (Co^{II})] \quad (1)$$

$$\dot{R} + XY \xrightarrow{K_{trap}} \begin{cases} R\text{-}X + \dot{Y} \\ OR \\ R\text{-}Y + \dot{X} \end{cases} \quad (2)$$

$$(Co^{II}) + \dot{X}/\dot{Y} \longrightarrow X\text{-}(Co^{III})/Y\text{-}(Co^{III}) \quad (3)$$

Scheme 2.

(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 side-products are obtained.

(5) Reactions carried out under thermal conditions in refluxing dichloromethane or benzene give the same products, but there are marked differences in the induction period, the subsequent reaction time, and, in a few cases, the yield of the products.

3. Discussion

3.1. Mechanism of trapping in organocobaloxime (1): a non-chain free radical process

The results presented above point clearly to a non-chain free radical route for the reaction of **1** with the radical precursor XY. The features of this mechanism (Scheme 2) are (i) homolysis of $R\text{-}Co^{III}$ (where R = $Ph\text{-}C{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}CH_2$) to give an inert radical pair containing $R^{\cdot}$ and (Co^{II}) (eqn. (1)); (ii) atom(group)

TABLE 1. Product formation from the reaction of $PhC{\equiv}CCH_2CH_2CH_2M$ [a] (**1**) with radical precursors XY

Entry	XY	No.	Time (h)	Organic product	No.	Yield [b]	Inorganic product	No.
1	CCl_4	**2a**	16	$PhC{\equiv}CCH_2CH_2CH_2Cl$	**3**	63	Cl_3CM	**4**
2	$BrCCl_3$	**2b**	10	$PhC{\equiv}CCH_2CH_2CH_2Br$	**5**	71	Cl_3CM	**4**
3	CCl_3CN	**2c**	12	$PhC{\equiv}CCH_2CH_2CH_2Cl$ + $PhC{\equiv}CCH_2CH_2CH_3$	**3** **6**	82 [c] 14 [c]	$NCCl_2CM$	**7**
4	PhSSPh	**2d**	15	$PhC{\equiv}CCH_2CH_2CH_2SPh$	**8**	80	PhSM	**9**
5	PhSeSePh	**2e**	14	$PhC{\equiv}CCH_2CH_2CH_2SePh$	**10**	69	PhSeM	**11**
6	PhTeTePh	**2f**	16	$PhC{\equiv}CCH_2CH_2CH_2TePh$	**12**	76	PhTeM	**13**
7	ArSCl [d]	**2g**	18	$PhC{\equiv}CCH_2CH_2CH_2SAr$	**14**	72	ClM	**15**
8	PhSeBr	**2h**	18	$PhC{\equiv}CCH_2CH_2CH_2SePh$ + $Ph\text{-}C(Br)=C(SePh)CH_2CH_2CH_2SePh$	**10** **16**	52 [e] 25 [e]	BrM	**17**

[a] M = $Co^{III}(dmgH)_2Py$. [b] Refers to % isolated yield with respect to cobaloxime (**1**). [c] Average yield from three experiments. [d] Ar = 2,4-(NO_2)-C_6H_3-. [e] Work-up after 10 h affords 69% of **10**, 9% of **16** and 16% of unreacted **1**.

transfer from XY by R in a bimolecular process (eqn. (2)), and (iii) coupling of (Co^{II}) with the counter radical (X or Y) formed in step (ii) (eqn. (3)).

The fact that the dimerized product resulting from R (*i.e.* R–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 and the rate of trapping (K_{trap}) is rather high. The formation of a single organic product in each of the reactions, except in the case of **2c** and **2h**, is also noteworthy, since it shows the high degree of chemoselectivity in these reactions.

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 as in eqn. (1), thereby totally inhibiting the radical trapping reaction (eqn. (2)).

The formation of ill-defined products in reactions conducted in the presence of oxygen is not surprising. It is generally known [4] that organocobaloximes undergo oxygen insertion under photostimulation to give $ROO(Co^{III})$ and the latter could react with XY in many ways.

3.2. Product distribution

The photostimulated reaction of cobaloxime **1** with various radical precursors **2a–2h** gives rise to interesting organic product distributions. For brevity in presentation, the reactions can be considered under the following three classes:

Case I: *Reactions involving halogen atom transfer from XY* (*where Y = Cl, Br*). As shown in entries 1–3 in Table 1, the reaction of organocobaloxime (**1**) with CCl_4, $BrCCl_3$ and CCl_3CN results in selective halogen atom abstraction from XY by the 5-phenylpent-4-ynyl radical. This is in contrast to earlier observations [5,6] on the reaction of allyl, allenyl, propargyl and even 3-phenyl-prop-2-ynyl cobaloximes with the above free radical precursors in which regiospecific formation of the carbon–carbon bond was found to take place by an S_H2 mechanism.

$$CH_3CH{=}CHCH_2(Co^{III}) + BrCCl_3 \longrightarrow CH_3(Cl_3C)CHCH{=}CH_2 + Br(Co^{III}) \quad (4)$$

$$PhC{\equiv}C{-}CH_2(Co^{III}) + \dot{C}H(CO_2Et)_2 \longrightarrow Ph[(CO_2Et)_2CH]C{=}C{=}CH_2 + (Co^{II}) \quad (5)$$

That similar carbon–carbon bond formation does not take place under our conditions suggests that in this case, the rate of halogen atom abstraction is rather high. Further details of the mechanism must await kinetic studies. The formation of the hydrocarbon **6** in moderately low yield in the reaction of **1** with trichloroacetonitrile (entry 3) deserves special mention. Initially, we assumed that hydrogen abstraction from the solvent might have resulted in the formation of **6**. However, when we carried out the reactions in chloroform and benzene, we detected no hexachloroethane and bibenzyl (possible products in the case of hydrogen atom abstraction from the solvent) even when the reactions were carried out at a high reactant concentration (1 mol l^{-1}). The possibility of hydrogen radical abstraction from dissolved water in the system cannot be completely ruled out [7*] even though we obtained nearly identical product distributions by repeating the reaction using anhydrous dichloromethane having a 0.005% water content, which corresponds to a concentration of about 3 mmol l^{-1}. An alternative explanation involves hydrogen abstraction by R˙ from the equatorial dimethylglyoximato ligand (dmgH) of the parent cobaloxime [6]. We are not clear, however, why partial formation of **6** is observed only in the reaction with **2c** and not with the other radical precursors.

Case II: *Reactions involving heteroatom containing group transfer from XY* (*where X = Y = PhQ; Q = S, Se, Te*). Diphenyldichalcogenides are known to be very effective radical trapping agents [8]. This is confirmed by our present results showing that 5-phenylpent-4-ynyl sulfide, selenide and telluride (**8**, **10**, **12**) are formed in the reactions of **1** with **2d–2f**.

Case III: *Reactions involving heteroatom containing group transfer from XY* (*where Y = Cl, Br*). Reaction of **1** with **2g** and **2h** selectively promotes transfer of the group "X" to give rise to **14**, **10** and **16**. These results are in sharp contrast to those in Case I, where halogen atom transfer from the carbon–halogen bond is observed. The formation of products **14**, **10**, and **16** can be considered either in terms of the mechanism discussed earlier or of an alternative non-chain mechanism which involves prior abstraction of halogen atom from X–Y by cobaloxime(II) and subsequent coupling of Ṙ and Ẋ (eqns. (6) and (7)).

$$(Co^{II}) + XY \longrightarrow Y(Co^{III}) + \dot{X} \quad (6)$$

$$\dot{R} + \dot{X} \longrightarrow RX \quad (7)$$

The above mechanism gains some support from the fact that cobaloxime(II) is known to abstract halogen from heteroatom–halogen bonds.

Finally, the formation of 5-bromo,5-phenylpent-4-enyl 1,4-bis(phenyl selenide) (**16**) in the reaction of **1** with **2h** can be ascribed to the reaction of **10** with phenylselenyl bromide. Independent experiments with **10** and **2h** confirmed this.

* Reference number with asterisk indicates a note in the list of references.

4. Experimental details

All chemicals used were commerical products (Aldrich) and were distilled or recrystallized prior to use. AR grade dichloromethane (99%) was refluxed over P_2O_5 under nitrogen and distilled prior to use (water content $< 0.05\%$). Reaction of **2c** was additionally carried out in dichloromethane (anhydrous, 99 + %, Aldrich, water $< 0.005\%$). All operations were performed by standard Schlenk techniques under dry extra-pure nitrogen. The ^1H (200 MHz) and ^{13}C (54 MHz) NMR spectra of all compounds were recorded in $CDCl_3$ on a Gemini-200 spectrometer. Chemical shifts (δ) were measured relative to internal TMS. Mass spectra (MS) were obtained at 70 eV with a Finnigan MAT-1020B instrument; principal ions along with their relative abundance are reported. IR spectra were recorded on a Nicolet-740 FTIR spectrometer.

4.1 Synthesis of 5-phenylpent-4-ynyl cobaloxime

Cobaloxime (**1**) was prepared by the published procedure [9] involving reaction of $Co^I(dmgH)_2Py$ with $PhC{\equiv}CCH_2CH_2CH_2Br$ under nitrogen at 5°C, and was recrystallized from an ethyl acetate/hexane (1 : 1 v/v) mixture. ^1H NMR($CDCl_3$): δ 0.94 (m, 2H); 1.58 (t, 2H); 2.15 (s, 12H); 2.29 (t, 2H); 7.41, 7.73, 8.62 (m, 5H). Anal. Found: C, 56.48; H, 5.79. $C_{24}H_{30}N_5O_4Co$ calcd.: C, 56.36; H, 5.91%.

4.2. General method of photolysis

A solution of **1** (0.3 g, 0.73 mmol) in degassed dichloromethane (20 ml) was placed in an all Pyrex double-walled vessel under nitrogen and was externally cooled to 0°C by use of a thermostated refrigerated circulator, model mgw-LAUDA RK-20. A solution of the radical precursor XY (1.1 mmol) in deaerated dichloromethane (10 ml) was added with constant stirring and the mixture was irradiated with a 500 W sun lamp placed 5 cm away from the reaction vessel. After completion (TLC monitoring) of the reaction, the mixture was brought to room temperature and concentrated under reduced pressure. Flash chromatographic separation on silica gel initially with pentane and then with dichloromethane as eluant afforded the pure organic products. Inorganic products were eluted with a dichloromethane/ethyl acetate (1 : 1 v/v) mixture. The product distributions are summarized in Table 1.

4.3. Spectral characteristics of the products

Trichloromethyl bis(dimethyl glyoximato)(pyridine) cobalt(III) (**4**). Red solid. ^1H NMR: δ 2.40 (s, 6H); 2.42 (s, 6H); 7.22, 7.70, 8.24 (m, 5H). Anal. Found: C, 34.44; H, 3.80. $C_{14}H_9N_5O_4Cl_3Co$ calcd.: C, 34.56; H, 3.94%.

Cyanodichloromethyl bis(dimethylglyoximato)(pyridine) cobalt(III) (**7**). Red solid. ^1H NMR: δ 2.3 (s, 12H); 7.31, 7.76, 8.43 (all m, 5H). Anal. Found: C, 37.71; H, 3.90. $C_{15}H_{19}N_6O_4Cl_2Co$ calcd.; C, 37.76; H, 4.01%.

5-Phenylpent-4-ynyl (phenyl) sulfide (**8**). Colourless oil. ^1H NMR: δ 1.93 (m, 2H); 2.55 (t, 2H); 3.07 (t, 2H); 7.08–7.50 (m, 10H). ^{13}C NMR: δ 18.4, 28.1, 32.5, 81.5, 88.8, 125.9, 127.2, 127.9, 128.1, 128.5, 128.8, 129.1, 131.5. MS: *m/e* (rel. int.): 252(3), 143(14), 129(79), 115(100), 109(19), 101(52), 77(21). IR (neat): 475w, 682m, 751m, 905w, 1025w, 1075w, 1090w, 1260w, 1434m, 1480m, 1583m, 1734w, 1895b, 1960w, 2850w, 2934b, 3049w, 3080w cm^{-1}. Anal. Found: C, 81.12; H, 6.28. $C_{17}H_{16}S$ calcd.: C, 80.91; H. 6.39%.

5-Phenylpent-4-ynyl (phenyl) selenide (**10**). Colourless oil. ^1H NMR: δ 1.95 (m, 2H); 2.55 (t, 2H); 3.05 (t, 2H); 7.08–7.50 (m, 10H). ^{13}C NMR δ 19.6, 26.8, 29.2, 81.7, 88.9, 126.8, 127.7, 128.2, 129.1, 130.2, 131.6, 132.7. MS: *m/e* (rel. int.): 300(29), 157(67), 143(31), 141(21), 128(50), 115(100), 102(14), 91(69), 77(38). IR (neat): 468w, 687s, 725s, 749m, 1017w, 1468w, 1242w, 1335w, 1434s, 1476s, 1575m, 1600w, 1730b, 1880w, 1938w, 2851w, 2925b, 3050w cm^{-1}. Anal. Found: C, 68.37; H, 5.21. $C_{17}H_{16}Se$ calcd.: C, 68.23; H, 5.39%.

5-Phenylpent-4-ynyl (phenyl) telluride (**12**). Yellow oil. ^1H NMR: δ 1.98 (m, 2H); 2.50 (t, 2H); 3.01 (t, 2H); 7.0–7.6 (m, 10H). Anal. Found: C, 58.55; H, 4.51. $C_{17}H_{16}Te$ calcd.: C, 58.66; H, 4.68%.

5-Phenylpent-4-ynyl (4,4-dinitro phenyl) sulfide (**14**). Orange yellow oil. ^1H NMR: δ 2.18 (m, 2H); 2.69 (t, 2H); 3.06 (t, 2H); 7.18–7.50 (m, 5H); 8.25–8.69 (m, 2H); 9.09 (m, 1H). MS: *m/e* (rel. int.): 342(8.5), 221(17), 175(39.3), 141(53), 128(53), 117(100), 114(72), 91(25.5), 77(27.66). IR (neat): 695–760m, 830m, 912m, 1050m, 1350s, 1530s, 1597s, 2360vw, 2852m, 2933m.

5-Bromo,5-phenylpent-4-enyl 1,4 *bis(phenyl selenide)* (**16**). Pale yellow oil. ^1H NMR: δ 2.00 (m, 2H); 2.60 (t, 2H); 2.86 (t, 2H); 7.16–7.50 (m, 15H). MS: *m/e* (rel. int.): 536(0.64), 457(24.64), 379(100), 157(45.45), 141(68.83), 128(46.75), 115(97.40), 91(26.62), 77(20.78). IR (neat): 517w, 690s, 737s, 1012w, 1035s, 1067w, 1372w, 1427s, 1466s, 1592s, 3907w, 2918b, 3090w.

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