Tetrahedron Vol. 41, No. 19, pp. 4095 to 4106, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

ALLYLATION AND OXIDATION REACTIONS PROMOTED BY COBALT(II) COMPLEXES.

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(*Received in Germany* 18 *February* 1985)

Abstract: Two examples of radical reactions involving cobalt complexes are described. The first one concerns the reactions of allylcobaloximes with 2-bromo 2-phenylacetonitriles leading to the corresponding monoallyl derivatives. It is shown that both the rate and regioselectivity of the reactions are affected by the nature of the substituents on the phenyl group: electron-withdrawing groups give higher rates and highly regiospecific reactions. The second type of radical reaction which finds useful synthetic applications is the oxidation of phenols by O_2 catalyzed by Schiff base cobalt complexes. By choosing carefully the catalyst and the solvent, these oxidations can be highly selective, quinones being the major oxidation products in most cases.

The use of transition metal complexes in organic synthesis has seen considerable developments in the last ten years. In these reactions, which can be either stoichiometric or catalytic, the organic substrates are most often involved as π ligands which undergo electrophilic or nucleophilic attack by various reagents. Radical reactions of synthetic utility using transition metal complexes are by contrast scarce. Cobalt complexes related to vitamin B_{12}: cobalamins, cobaloximes (bis-dimethylglyoximatocobalt), Schiff base or porphyrin complexes, are of great interest in that respect because the metal ion can exist in three different oxidation states: I, II, III, which in most cases can be easily interconverted without having to use strong oxidising or reducing agents (1). Therefore it is not surprising to observe radical reactions occuring by radical chain or by single electron transfer mechanisms with these complexes, some of them being of great potential synthetic utility because of their high chemo- or regioselectivity.

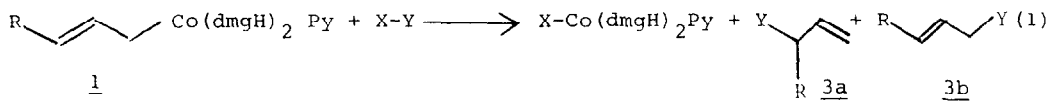
At the monovalent state, the cobalt ion of these complexes is a strong nucleophile which can react with various organic electrophiles leading to organocobalt complexes. Among these, σ-allyl complexes, such as the allylcobaloximes 1, are of great interest: they are easily prepared from allyl halides or dienes and their weak Co-C bond makes possible the transfer of the allyl group from cobalt to a suitable organic acceptor via radical chain reactions (2).

On the other hand, the cobalt(II) complexes have been known for several years for their oxygen-binding ability (3). Beside their importance as models of biological oxygen carriers, these complexes are good catalysts for the oxidation of various organic substrates: phenols (4,5) or indoles (6,7) by dioxygen. Their efficiency can be best explained by their aptitude to act as electron relay between the organic substrates and the O_2 molecule.

In this paper, we report 1) an extension of the allylation reactions using allylcobaloximes to various α-bromonitriles and 2) the use of cobalt(II) Schiff base complexes in the catalysis of new phenol oxidation reactions.

I. Allylation reactions of α-bromo nitriles.

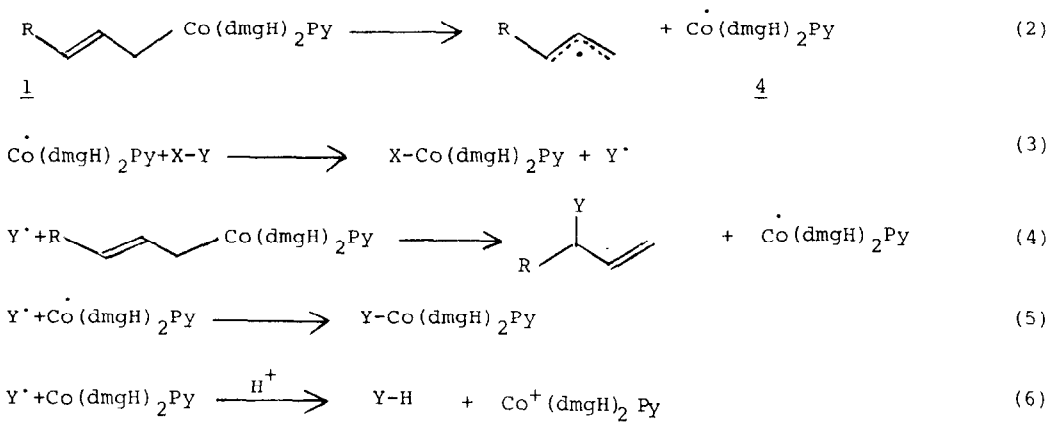
It has been previously reported (2) that allylcobaloximes 1 readily react with various halogenated organic compounds X-Y: polyhaloalkanes (8), sulfonyl halides (9), bromomalonic and bromo-3-acetoacetic esters (10), arylsulfenyl and arylselenyl chlorides (11), α-bromonitriles (12) to give allyl derivatives. During these reactions the allyl group initially bound to cobalt is transfered on the Y part of the halogenated X-Y substrate (eq.1):



dmgH : dimethylglyoximato

X : Br, Cl

These reactions most probably occur by a radical chain mechanism (2) in which cobaloxime(II) 4, formed by the homolytic cleavage of the cobalt-carbone bond of allylcobaloximes (eq.2) is the propagator of the chain (eq.3 and 4). Coupling or reduction reactions (eq.5 and 6) have been postulated as termination steps.



When the allyl group is substituted on the α-carbon atom (e.g. crotyl or 3,3-dimethylallyl), the major and, in most cases, single allylation product is compound 3a which results from the attack of the radical on the γ position (S_H2' reaction). The high regioselectivity of these reactions thus gives an easy access to a variety of organic derivatives having secondary or tertiary allyl substituents which are very difficult to prepare by more conventional methods, for example by nucleophilic displacements. Arylsulfenyl and arylselenyl chlorides (11) represent exceptions as they give rise selectively to allylthioethers or -selenoethers bearing the less substituted allyl groups.

So far, these allylation reactions have proved to be fast and reasonably efficient provided the halogenated organic derivatives could be easily reduced to radicals having strong electrophilic character. Their obvious synthetic utility has led us to try other free-radical precursors as possible substrates, in particular precursors of capto-dative radicals: these radicals which are substituted by both an electron-donating and an electron-withdrawing group, have shown (13) an unexpected stability and could therefore exhibit an interesting reactivity towards allylcobaloximes. An other extension of these reactions has been carried with using α-bromonitriles as precursors of either electrophilic or captodative radicals. The results reported now show that the latter are in fact much less reactive

towards the allylcobalt complexes than the former.

1) Reactions of allylcobaloximes with precursors of captodative radicals

Compounds 5, 6, 7 and 8 contain electron-withdrawing (ester or sulfone) or -donating (OCH_3 or SCH_3) groups bound to the carbon atom bearing the halogen substituent. Reactions with cobaloxime(II) 4 (eq.3) should give rise to the corresponding capto-dative radicals.

$CH_3OCHBrCO_2CH_3$ (5) $CH_3SCHBrCO_2CH_3$ (6) $CH_3SCHXSO_2CH_3$ (7 X = Br, 8 X = Cl)

Thermolysis of various allylcobaloximes 1 in the presence of these compounds gave mixtures of products among which the dehalogenated products: $CH_3OCH_2CO_2CH_3$, $CH_3SCH_2CO_2CH_3$ and $CH_3SCH_2SO_2CH_3$ respectively, were the major products (ca. 50%). The products resulting from the substitution of the Br or Cl atom by an allyl group were not formed in detectable amounts.

These results indicate that, though the capto-dative radical precursors are reactive under these conditions, the intermediate radicals are reduced by cobaloxime(II) (eq.6) faster than they give an S_H2' reaction with the allylcobalt complex (eq.4). As reactions were carried out using equimolar mixture of the complex and of the radical precursor, the yields in reduced product cannot exceed 50%.

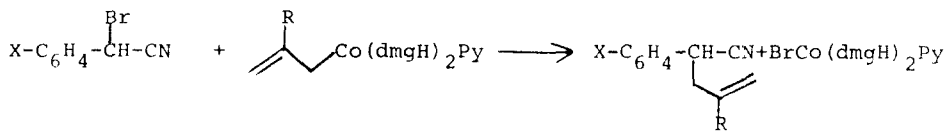
2) Reactions of allylcobaloximes with bromo-2 acetonitriles 9a-d

In order to confirm the above results and also to extend the allylation reactions to other halogenated derivatives, we looked at the reaction of allylcobaloximes with substituted bromo-2 phenyl-2 acetonitriles.

The reaction of α-bromonitriles with allylcobaloximes has been previously reported (12): only nitriles bearing two or three bromine atoms on the α position gave allylation products in satisfactory yields, probably because of the extra stabilization brought to the intermediate cyanoallyl radical by the bromine atoms.

Introducing a phenyl group on the α position will also increase the stability of the radical, which will be either capto-dative or electrophilic depending on the substituent present on the phenyl group.

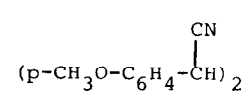
Allylcobaloxime 1a and 2-methyl allylcobaloxime 1b react with nitriles 9a-d to give the corresponding allylation products 10a-d and 11a-d respectively. Yields are all above 90% except with 9d which gives a mixture of allylation products 10d or 11d (70%) and of the diastereomeric dimers 12.



9 a X=H, b X=p-NO_2, c X=m-Cl, d X=p-OCH_3

1 a R=H, b R=CH_3

10 R=H, 11 R=CH_3



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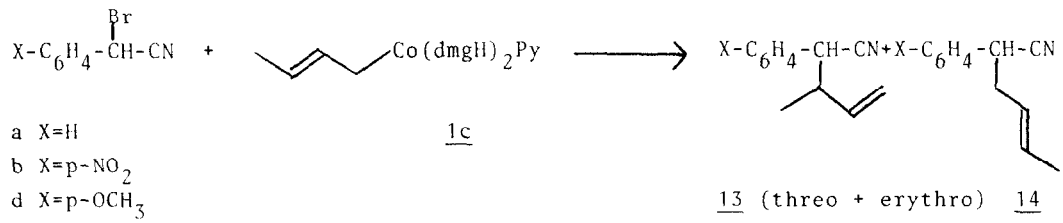
Significant variations are observed in the rates of reactions of the various nitriles: the highest rate is observed with the nitro-substituted nitrile 9b which reacts about 10 times faster with both allylcobaloximes 1a and 1b than the other nitriles. These results confirm that halogenated organic molecules which are precursors of electrophilic radicals are much more reactive towards allylcobaloximes than precursors of capto-dative radicals.

In order to examine how the structure of the radicals might affect the regiospecificity of the reaction, we studied the reactions of nitriles 9a,b and d with crotylcobaloxime 1c.



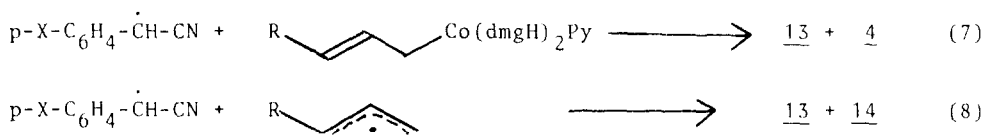
9 a X=H
b X=p-NO_2
d X=p-OCH_3

1c

13 (threo + erythro) 14

In the case of the nitro-substituted nitrile 9b, the reaction was regiospecific leading to a single product, 13b as 50:50 mixture of diastereoisomers. By contrast, the reactions of crotylcobaloxime 1c with nitriles 9a and 9d gave mixtures of isomeric compounds 13 and 14 in ratios which were respectively 70:30 and 50:50.

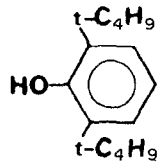
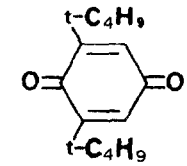
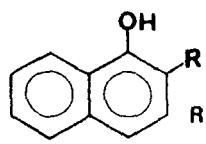
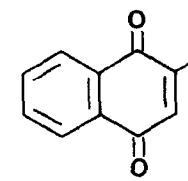
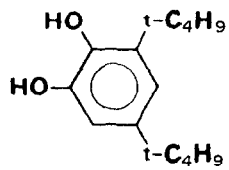
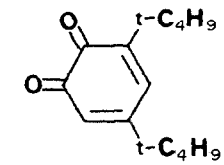
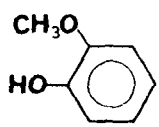
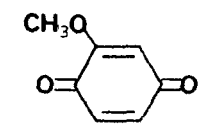
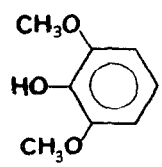
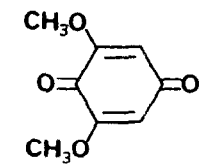
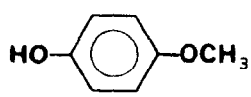
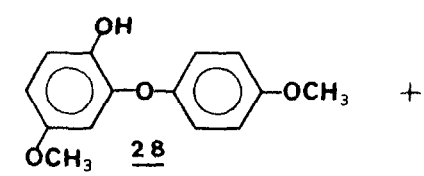
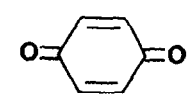
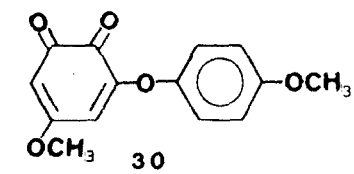
These results show that the regioselectivity of the allylation reactions depend markedly on the structure of the reacting nitrile. As mentioned previously, most of the allylation reactions using allylcobaloximes have proved to be regiospecific, the product of attack on the γ position of the allyl group being in nearly all cases the only reaction product. Two exceptions to this rule have been reported (9,10) where mixtures of the two possible isomers were obtained. The presence in thesecases of a significant amount of the isomer having the less substituted double-bond had been explained by steric hindrance of the radical attack at the γ position of the allyl group. This explanation does not hold in the present case because the steric effects should be the same for the three nitriles 9a, 9b and 9d. It seems more likely that the different regioselectivities are due to differences in the reactivities of the intermediate free radicals. The more electrophilic radical, obtained from nitrile 9b, is probably much more reactive towards the allyl group than the other two radicals. With the latter, the S_H2' reaction (eq.7) may become slower than the coupling between the phenylcyanomethyl and crotyl radicals (eq.8) and this will result in a mixture of the two isomers 13 and 14.



II. Oxidation of phenols by molecular oxygen catalyzed by Schiff-base cobalt(II) complexes.

The oxidation of phenols by molecular oxygen catalyzed by complexes of cobalt(II) and other transition metals is a well-known reaction which has been the subject of numerous studies (4,5) aiming at finding more efficient catalysts and at obtaining a better knowledge of their mechanism. There is now ample evidence(5) that these reactions involve several radical intermediates, the metal playing the role of an electron relay between the organic substrates and molecular oxygen. Surprisingly, the number of phenolic compounds on which these oxidation reactions

TABLE 1 : OXIDATION PRODUCTS

Phénol	Oxidation products
 15	 16
 R = H : 17 R = CH_3 : 19	 R = H : 18 R = CH_3 : 20
 21	 22
 23	 24
 25	 26
 27	 +
 29 +  30	

have been attempted is rather limited: they include hindered phenols such as di- and tri-alkyl phenols and 4-aryl phenols (14). Recently, we have reported (5) an extension of this catalytic oxidation to 1-naphtol and 2-methyl 1-naphtol. We wish to report more results which show that Schiff-base cobalt(II) complexes can oxidise both efficiently and selectively other phenolic derivatives, the ease of oxidation depending on the substrate and also on the nature of the catalyst and of the solvent used. The catalysts which were used in this study were either monomeric or polymeric Schiff-base cobalt complexes. The monomeric complexes include both tetradentate (CoSalen, CoSalpen) and pentadentate (CoSalN-Medpt)[*] complexes which, according to previous studies, can exhibit different selectivities towards the same phenolic substrate. The polymeric cobalt complex Co(polySaldpt) has been used already (5) to oxidise various phenols with O_2: it was obtained by covalently binding the SaldptH_2 Schiff-base to a Merrifield resin followed by cobalt insertion (15). The catalyst thus obtained showed some interesting features: insolubility, compatibility with several organic solvents, ease of recovery. Furthermore, it proved to be more stable, in the standard conditions of oxidation, than its monomeric analog which becomes progressively inactive, due probably to its degradation by peroxidic intermediates. However, the efficiency of the polymeric catalyst is much less than that of the monomeric one.

On tables 1 and 2 are gathered the results obtained in the oxidations of various phenols by O_2 in the presence of the cobalt complexes. We have also included, for the sake of comparison, results concerning 2,6 di-t-butylphenol, 1-naphtol and 2-methyl 1-naphtol which were previously published (5).

2,6-di-t-butylphenol 15, 1-naphtol 17 and 2-methyl 1-naphtol 19.

As mentioned previously, the three phenols are very good substrates for these oxygenation reactions. In most cases, a quantitative yield in the corresponding quinones is obtained. The rate of oxidation varies both with the catalyst, CoSalN-Medpt being the most efficient, and the solvent, acetonitrile proving to be very good solvent in general for these reactions.

3,5-di-t-butylcatechol 21

Oxidation of catechols by molecular oxygen can be catalyzed by copper (16), iron (17), vanadium (18) or ruthenium (19) salts. Depending on the catalysts, the oxidation products are either the orthobenzoquinones or, more often, a derivative of (Z,Z) muconic acid which is formed by the oxidative cleavage of the benzene ring. 3,5-di-t-butyl catechol was choosen as a substrate for the cobalt-catalyzed oxidation because its primary oxidation product, 3,5-di-t-butyl o-benzoquinone is stable, contrary to other o-benzoquinones, and can be more easily identified. This quinone is indeed the only oxidation product obtained in the cobalt-catalyzed oxygenation reactions, the Schiff-base cobalt complexes exhibiting the same selectivity as Mn or Fe Salen (20) or Mn, Co or Ni acetylacetonates (21).

Methoxyphenols 23, 25 and 27

The rates and products of oxidation of methoxy-substituted phenols depend greatly on the number and position of the OCH_3 substituents and on the oxidant used: not only o- or p-benzoquinones can be obtained, but also dimeric or polymeric oxidation

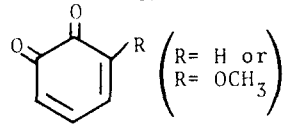
[*] Salen = bis(salicylidene) ethylenediamine
Salpen = bis(salicylidene) propylendiamine
SalN-Mdpt = bis (3,3'-salicylidene)Nmethyl dipropylenetriamine.

TABLE 2: OXIDATION OF PHENOLS BY O_2 CATALYZED BY SCHIFF-BASE COBALT COMPLEXES.

Phenol	Catalyst [a]	Solvent	Reaction time (hr)	Yield	Oxidation products (%)
15	Co(Salen)	CH_3OH	2	100	16 : 100
	Co(SalN-Medpt)	CH_3CN	1	100	16 : 100
	Co(SalN-Medpt)	toluene	6	100	16 : 100
	Co(polySaldpt)	toluene	6	100	16 : 100
17	Co(SalN-Medpt)	CH_3CN	0.5	100	18 : 100
	Co(polySaldpt)	CH_3CN	24	80	18 : 50
19	Co(SalN-Medpt)	toluene	0.5	100	20 : 100
	Co(polySaldpt)	toluene	0.5	100	20 : 100
21	Co(Salpen)	CH_3CN	0.75	100	22 : 100
	Co(SalN-Medpt)	toluene	0.5	100	22 : 100
	Co(polySaldpt)	tolune	0.5	100	22 : 100
23	Co(Salen)	CH_3OH	24	90	24 : 100
	Co(SalN-Medpt)	toluene	24	93	24 : 100
	Co(polySaldpt)	toluene	24	10	24 : 100
25	Co(Salen)	CH_3OH	1	100	26 : 100
	Co(SalN-Medpt)	toluene	3	100	26 : 100
	Co(polySaldpt)	toluene	24	35	26 : 100
	Co(Salen)	CH_3OH	24	60	29 : 35 30 : 65
	Co(SalN-Medpt)	CH_3CN	24	20	28 : 40 30 : 60
	Co(SalN-Medpt)	toluene	24	30	28 : 80[d]
	Co(polySaldpt)	toluene	24	40	28 : 80[d]

a (catalyst)/(substrat) = 0.1
b based on oxidised phenol.
c various other unidentified products are formed in addition to the naphthoquinone (18). The products might be dimeric products (5).
d 4-methoxy o-benzoquinone is the other reaction product but has not been obtained in pure state.

products in which two or more phenolic rings are linked by C-O or C-C bonds, and products resulting from oxidative demethylation: thus, 2-methoxyphenol 23 and 2,6-dimethoxyphenol 25 are oxidised by $NaIO_4$ to the corresponding o-benzoquinones



whereas in the same conditions 4-methoxyphenol 27 gives rise to p-benzoquinone (22) which can also be obtained by anodic oxidation (23). Use of $Pb(OAc)_4$ as an oxidant leads to p-benzoquinones with the same substrates (22, 24). Products of oxidative coupling are favored when the oxydant is either $K_3Fe(CN)_6$ (25) or O_2 in basic conditions (26).

In the presence of Schiff-base cobalt(II) complexes, 2-methoxy phenol 23 and 2,6-dimethoxyphenol 25 are oxidised by O_2 to the corresponding p-benzoquinones 24 and 26 respectively. This is not surprising as cobalt-catalyzed oxygenations are known to give predominantly products oxidised at the para position. The polymeric complex also catalyzes these oxidations but, as expected, much less efficiently than its monomeric counterpart.

Oxidation of 4-methoxyphenol 27 proved to be much less selective and therefore to be of lesser synthetic value. From the complex reaction mixture we were able to isolate and identify the following products:

- the p-benzoquinone 29
- the o-quinone 30 which results from the coupling of the starting phenol and 4-methoxy o-benzoquinone which could be detected in small amounts in some of the experiments.
- compound 28 which is probably formed by coupling of two phenoxy radicals followed by tautomerisation of the intermediate. Similar coupling products have been observed before in the oxidations of alkyl 4-methoxy phenols by $K_3Fe(CN)_6$ in basic conditions (27), but with this oxidant, they undergo further oxidation to dioxepinones.

It is interesting to note that, though less efficient and selective in this case than other oxidising systems, the cobalt-O_2 system, because of its mild oxidising power, allows the obtention of products which, with stronger oxidants, are converted to more oxidised derivatives.

Finally 3-methoxyphenol and 3,5-dimethoxy could not be oxidised by the cobalt-O_2 system. This is not too surprising in view of the fact that 3-methoxyphenol is not readily oxidised even by $NaIO_4$ (22).

Conclusion

Cobalt complexes can participate in highly selective radical reactions. Both the allylation reactions and the oxygenation reactions are carried out under very mild conditions which makes them quite useful in organic synthesis. Extension of both reactions to other organic substrates is under way.

EXPERIMENTAL

IR spectra were measured on a Beckman Acculab 10 spectrometer, UV-visible spectra on a Beckman 25 spectrometer and NMR spectra on a Perkin Elmer R-32 (90MHz) spectrometer in $CDCl_3$ solution containing TMS as internal reference. Mass spectra were measured on a Ribermag R-10 spectrometer.

Starting materials

(Pyridine) cobaloxime (II) was synthetised by Schrauzer's method (28) and the complexes Co(Salen), Co(Salpn) and Co(SalN-Medpt) prepared according to published procedure (29). The synthesis of polymeric Schiff-base cobalt complexes

has been described previously (15). Co(polySaldpt) was prepared from Merrifield polymer Biobeads SXI and contained 0.5 mmol equiv. of cobalt per gram. Allylcobaloximes 1a-1d have been synthetized according to published procedures (30)

General procedure for the synthesis of 2-bromo 2-phenylacetonitriles 9a - 9d

In a two-necked flask equipped with a condenser and dropping funnel, 0.1mole of the starting nitrile are dissolved in 75ml of CCl_4. 6ml of the Br_2 dissolved in 100ml of CCl_4 are added to this solution under irradiation with two 250W tungsten lamps. At the end of the reaction, the solvent is removed under vacuum and the brominated product identified by its NMR spectrum. The signal of the -CHBr-proton appears at: δ = 5.57 (9a), 5.50 (9b), 5.45 (9c) and 5.50 ppm (9d). Yields: 91-94% 9d: MP = 45°5 - 46°5.

Reactions of allylcobaloximes with 2-bromo 2-phenylacetonitriles 9a - 9d.

In a typical experiment, 1 mmol of allylcobaloxime and 1.2 mmol of 2-bromo-2 phenylacetonitrile 9 are dissolved in 5ml of degassed CH_2Cl_2. The reaction mixture is left at room temperature for 2 hours. At the end of the reaction the solvent is removed under vacuum and the reaction products are purified by chromatography on a Silicagel column using a mixture of CH_2Cl_2/acetone (9:1) as eluting solvent. The structures of the organic products have been determined from their NMR and mass spectra (Table 3). 2-bromo-2-phenylacetonitriles 9a - 9d and their allylation products all show a weak band at 2220 cm^{-1} (ν_{CN}) in their IR spectra.

General procedure for the oxidation of phenols.

To a solution of the starting phenol (0.1M) in the appropriate solvent was added the cobalt complex (0.01M). The solution was stirred in a two-necked flask connected to a gas-burette filled with oxygen (pressure 1.2 atm.) and the oxygen consumption was measured under constant pressure (1 atm.) at regular intervals. At the end of the reaction the solvent was evaporated off under reduced pressure and the products were separated by chromatography on a silica gel column (Merck CC7). For reactions carried out with the polymeric complex, the catalyst was removed by filtration. 28 and 30 were purified using h.p.l.c under the following conditions: solvent $CHCl_3$ - CH_3OH (98:2), column: ultrasphere Si (l: 25cm, d: 1cm); pressure 2000 psi. The quinones 16, 18, 20, 22 and 29 were characterised by comparison of their properties with those described in the litterature. The para benzoquinones 24 and 26 and the coupling products 28 and 30 were identified by their spectroscopic data (Table 4), their elemental analysis and mass spectra.

Elemental analysis

24: found C, 61; H, 4.4; $C_7H_6O_3$ requires C, 60.87; H, 4.35.

26: found C, 57.55; H, 4.95. $C_8H_8O_4$ requires C, 57.14; H, 4.76.

28: found C, 68.58; H, 5.75. $C_{14}H_{14}O_{14}$ requires C, 68.29; H, 5.69.

30: found C, 65.54; H, 4.91. $C_{14}H_{12}O_5$ requires C, 64.61; H, 4.61.

Mass Spectra

* 24 and 28: Gas phase chromatography/mass spectrometer.

24: 54(M-$C_4H_4O_2$, 70.8%), 69(M-CH_3-C_3H_2O, 100%), 110(M-CO, 53%) 138(M, 51,3%).

28: 108(M/2-CH_3, 100%), 246(M,83,4%).

* 26 and 30: chemical ionization/desorption (reagent gas NH_3).

26: 169(M+1, 99%), 186(M+18, 100%).

30: 232(M-CO, 16.4%), 261(M+1, 100%), 278(M+18, 34%).

TABLE 3 : SPECTRAL DATA OF ALLYL SUBSTITUTED PHENYLACETONITRILES.

compound	reaction time, temperature and yield	Ha	Hb	Hc	R_1	R_2	R_3	H_{Ph}	Mass Spectrometry m/z
10a	2h - 20°C - 95%	3.85(t)	2.66(t)	5.25(m)	2.66(t)	5.85(m)	5.25(m)	7.42(m)	157(M^+),116
10b	1h - 20°C -97%	4.12(t)	2.70(t)	5.20(m)	2.70(t)	5.85(m)	5.20(m)	7.92(dd)	202(M^+),151
10c	2h - 20°C - 95%	3.75(t)	2.60(q)	5.15(m)	2.60(q)	5.80(m)	5.15(m)	7.30(dn)	191(M^+),150
10d	2h - 20°C - 80%	3.80(t)	2.60(t)	5.17(m)	2.60(t)	5.70(m)	5.17(m)	7.00(dd)	187(M^+),146
11a	2h - 20°C - 80%	3.98(q)	2.60(m)	4.95(s)	2.60(m)	1.80(s)	4.85(s)	7.42(m)	170(M^+-1)55
11b	1h - 20°C - 97%	4.13(t)	2.66(q)	4.96(s)	2.66(q)	1.82(s)	4.85(s)	8.02(dd)	216(M^+),55
11c	2h - 20°C - 95%	3.90(t)	2.60(m)	4.95(s)	2.60(m)	1.78(s)	4.85(s)	7.30(m)	205(M^+),55
11d	2h - 20°C - 80%	3.85(q)	2.55(q)	4.90(s)	2.55(m)	1.75(s)	4.87(s)	7.08(m)	201(M^+),146
13a	2h - 20°C - 92%	3.82(t)	2.63(m)	5.10(m)	1.15(d,d)	5.80(m)	5.10(m)	7.35(m)	171(M^+),117
14a	2h - 20°C - 92%	3.75(m)	2.50(m)	5.50(m)	2.50(m)	5.50(m)	1.65(d)	7.40(m)	171(M^+),117
13b	1h - 20°C - 83%	4.00(m)	2.62(m)	5.12(m)	1.15(d,d)	5.72(q)	5.12(m)	7.9(q)	216(M^+),55
13d	2h - 20°C - 85%	3.48(m)	2.58(m)	5.15(s)	1.10(d,d)	5.78(m)	5.05(t)	7.04(dd)	201(M^+),146
14d	2h - 20°C - 85%	3.64(t)	2.40(t)	5.52(m)	2.40(t)	5.52(m)	1.66 (d)	6.70(d,d)	201(M^+),146

TABLE 4: SPECTRAL DATA OF OXIDATION PRODUCTS.

Spectral data	Product			
	24	26	28	30
δ_H (ppm) C=CH	6.75(2H), 5.98(1H)	5.77	-	5.82, 5.5
δ_H (ppm) Ar	-	-	6.3 - 6.9	7
δ_H (ppm) OH	-	-	5.3	-
δ_H (ppm) OCH_3	3.86	3.79	3.7, 3.58	3.35, 3.8
$\nu_{max}(cm^{-1})$	1600, 1660	1640, 1690	1600, 1500, 3530	1650, 1670, 1590, 1500
$\lambda_{max}(nm)$	355, 250	376, 285	275, 248.5	340(s), 278.5 230

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