

Scheme 2. (a), $R^1 = H$, $R^2 = C_6H_5$; (4a):(5a):(6a) = 78:7:15. (b), $R^1 = C_6H_5$, $R^2 = H$; >98% (6b) (see Table 1).

Table 1. γ -Lactones of types (2), (4), (5), and (6) [a] prepared.

Cpd.	R^1	R^2	M. p. [$^{\circ}C$] B. p. [$^{\circ}C$ /torr]	$\tilde{\nu}_{(C=O)}$ [cm^{-1}]
(2a)	H	C_6H_5	92–92	1765
(2b)	C_6H_5	H	84–85	1770
(2c)	H	$C(CH_3)_3$	100–110/0.1	1765
(2d)	H	SC_6H_5	150–160/0.1	1765
(2e)	H	OC_6H_5	74–75	1765
(4a) [b]	H	C_6H_5	50–51	1765
(5a) [b]	H	C_6H_5	90–100/0.1	1770
(6a) [b]	H	C_6H_5	90–100/0.1	1770
(6b)	C_6H_5	H	90–100/0.1	1770

[a] Yield 94–98%; all compounds gave correct CH analyses. The configurational assignment of the γ -lactones was based on 1H -NMR spectra; thus we found that in *cis-trans* isomeric γ -lactones always $J_{3,4-cis} < J_{3,4-trans}$ and $\tau(cis-4-CH_3) > \tau(trans-4-CH_3)$. Cf. also D. Sawostianoff, M. Pfau, Bull. Soc. Chim. Fr. 1967, 4162.

[b] Yield (4a) + (5a) + (6a) = 97%.

Meerwein carbenium-ion mechanism because such a process should involve at least partial rotation about the C^3-C^4 bond in the case of the *cis*-lactones (1b) and (3b). We therefore assume that ring opening and migration of CH_3 or H are part of a concerted dyotropic rearrangement^[5]. This assumption is further supported by two experimental results: (i) the reaction of (1a) with isopropylmagnesium bromide gives not only the Grignard adduct at the carbonyl group (5-hydroxy-2,6,6-trimethyl-4-phenyl-3-heptanone) but also considerable amounts of (2a). The $MgBr_2$ generated in the Schlenk equilibrium^[6] initiates the ring expansion of (1a); if a carbenium ion were an intermediate it should be trapped by the organometallic species. (ii) In the reaction of 1 equiv. of $MgBr_2$ with *cis*-3-methyl-4-phenyl-2-oxetanone ring expansion cannot occur; instead, decarboxylation gives a quantitative yield of *trans*-1-phenylpropene. The carbenium ion apparently formed in this case decomposes *via* rotation and CO_2 elimination, *i.e.* reactions which are not observed with ring-expanding β -lactones.

Procedure

3.2 M $MgBr_2$ -ether (1.55 ml, 4.9 mmol) is added to a water-cooled stirred solution of (1a) (1.00 g, 4.90 mmol) in anhydrous ether (10 ml). After 5 min, water (10 ml) is added and crystalline (2a) (98%) is isolated from the dried ether phase.

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(1a), 71647-83-1; (1b), 71647-84-2; (2a), 71647-85-3; (2b), 71647-86-4; (2c), 71647-87-5; (2d), 71647-88-6; (2e), 71647-89-7; (3a), 70982-88-6; (3b), 71647-90-0; (4a), 20215-56-9; (5a), 71647-91-1; (6a), 71647-92-2; (6b), 71647-93-3

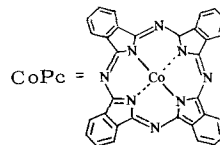
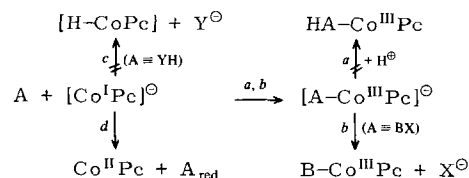
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Cobalt(I)-phthalocyanine Anion as Vitamin B₁₂ Model: Selectivity in Reactions with Electrophiles

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In order to understand vitamin B₁₂-catalyzed reactions^[1,2] and to ascertain the scope of the cobalt(I)-phthalocyanine anion $[Co^I Pc]^-$ as a stable reagent in synthetic chemistry (protecting group technique for syntheses of peptides^[3a] and β -lactam antibiotics^[3b], intermediate in the production of blue dyes^[3c]), it is important to know the selectivity of this anion towards functional groups. Owing to the extremely high reactivity of cobal(I)amine^[4] and its model compounds cobal(I)oxime^[4] and $[Co^I Pc]^{5-}$ towards alkyl halides they are designated as "supernucleophiles".

We have now found that the cobalt(I)-phthalocyanine anion (as lithium salt $Li[Co^I Pc]$) behaves as a supernucleophile in nucleophilic substitution of acyl compounds (2a) and (2b) (reaction b), while no nucleophilic additions (reaction a) were observed with carbonyl compounds (1), including those with cumulated double bonds. Vinyl and aryl halides such as (2c) and (2d) do not undergo nucleophilic substitution (see Scheme 1 and Table 1).



Scheme 1. Reactions of compounds A with the cobalt(I)-phthalocyanine anion. See text for details.

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Table 1. Reaction of Li[Co^IPc] with compounds A in methanol or acetonitrile at 20 °C. Only compounds (2a), (2b), (4a), and (4b) react with [Co^IPc]⁻.

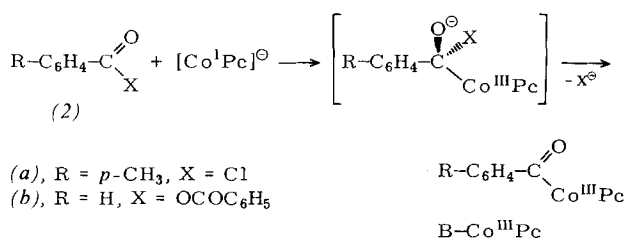
Compounds A No. Type	Reaction	Solvent	Reaction time	Stirring time [h]	Oxid. of Co ^I +/−	A	Yield [%] of isolated material			
							Reactants [Co ^I Pc]	CoPc complexes	Products X ⁻ or A _{red}	
(1a)	<i>n</i> -C ₆ H ₅ CHO	<i>a</i>	MeOH	[b]	144	−	68 [c]	99	0	—
(1b)	C ₆ H ₅ CHO	<i>a</i>	MeOH	[b]	48	−	99 [d]	99	0	—
(1c)	CH ₂ =CH COOC ₂ H ₅	<i>a</i>	MeOH	[b]	48	−	[e]	100	0	—
(1d)	C ₆ H ₅ N=C=O	<i>a</i>	MeCN	[b]	48	−	(91) [f]	99	0	—
(1e)	O=C=O	<i>a</i>	MeCN	[b]	960	−	—	93	0	—
(2a)	BX <i>p</i> -CH ₃ C ₆ H ₄ COCl	<i>b</i>	MeCN	< 1 min	2	+	0	0	100 B	Co ^{III} Pc 97 X [g]
(2b)	BX (C ₆ H ₅ CO) ₂ O	<i>b</i>	MeCN	3 h	3–96	+	5–8 [h]	0	99 B	Co ^{III} Pc 69–85 X [i]
(2c)	BX C ₆ H ₅ COOCH ₂ CF ₂ CH ₂	<i>b</i>	MeOH	[b]	144	−	92	100	0	0
(2d)	BX C ₆ H ₅ Cl	<i>b</i>	MeOH	[b]	288	−	87	96	0	0
(3a)	YH C ₆ H ₅ OH	<i>c</i>	MeCN	[b]	4	−	100	100	—	0
(3b)	YH (C ₆ H ₅ OCO) ₂ CH ₂	<i>c</i>	MeCN	[b]	120	−	71	100	—	0
(4a)	C ₆ H ₅ NO ₂	<i>d</i>	MeOH	2 min	1.5	+	0	0	102 Co ^{II} Pc	(A _{red}) [j]
(4b)	<i>p</i> -Cl C ₆ H ₄ NO	<i>d</i>	MeOH	20 h	72	+	0	0	98 Co ^{II} Pc	[k]
(4c)	CH ₃ C≡N	<i>d</i>	MeCN	[b]	720	−	[l]	98	0	0
Alkyl halides [5b]		(<i>b</i>)	MeOH	< 1 min to 60 min	[5b]	+	0	0	[5b]	[5b]

[a] Gravimetrically as Co^{II}Pc after air-oxidation. [b] See text. [c] Gravimetrically as *n*-butyraldehyde 2,4-dinitrophenylhydrazone together with 17% of 2-ethyl-2-hexenal 2,4-dinitrophenylhydrazone. [d] Gravimetrically as benzaldehyde 2,4-dinitrophenylhydrazone. [e] Neither A nor products thereof were detected. [f] 91% of triphenyl isocyanurate. [g] Volumetrically according to Mohr. [h] 8% of (2b) were isolated after 3 h, and 5% after 96 h. [i] Gravimetrically as benzoic acid. [j] Product mixture, principal component C₆H₅ NO (from IR). [k] Reduction products not yet elucidated. [l] MeCN as reactant and solvent.

(1a), (1b), and (1c) do not react with [Co^IPc]⁻ according to path *a*, neither under standard conditions for aldol condensations and Michael additions nor on 48 h refluxing in methanol. The aldehydes can be recovered as 2,4-dinitrophenylhydrazones; (1a) forms 17% of the aldol condensation product within 144 h. Nor does a Cannizzaro reaction occur under these conditions—thus indicating the low basicity of the supernucleophile [Co^IPc]⁻. Only on reaction of benzaldehyde (1b) with [Co^IPc]⁻ in 1,4-butanediol (150–170 °C, 72 h) can 30% of benzyl alcohol be isolated.

Likewise, no addition (reaction *a*) to the cumulated double bonds of phenyl isocyanate (1d) and carbon dioxide (1e) took place; (1d) undergoes quantitative trimerization to triphenyl isocyanurate.

In contrast, [Co^IPc]⁻ reacts very fast with *p*-toluoyl chloride (2a) and benzoic anhydride (2b), reaction with (2a) being at least 10³ times faster than with (2b). This behavior accords with the basicity of the leaving groups chloride and benzoate in an addition-elimination reaction. The acylated complexes *p*-toluoyl- and benzoyl-cobalt(III)phthalocyanine



(type B -Co^{III}-Pc) have been characterized by elemental analysis and IR spectra ($\nu(\text{C}=\text{O}) = 1740 \text{ cm}^{-1}$). The complexes, LiCl, and Li-benzoate can be isolated in quantitative yield.

2-Bromoallyl benzoate (2c) and chlorobenzene (2d) are completely inert toward nucleophilic attack by [Co^IPc]⁻ and are recovered quantitatively. The fact that no substitution occurs at the sp² carbon is a further criterion for the S_N2 character of the nucleophilic substitution reactions of [Co^IPc]⁻ with alkyl halides^[5b].

The acidic compounds phenol (3a) and diethyl malonate (3b) do not react according to path *c*, but can be recovered quantitatively.

Nitrobenzene (4a) is reduced very fast, according to reaction *d*, to nitrosobenzene, which itself, like 1-chloro-4-nitrosobenzene, can be slowly reduced further by [Co^IPc]⁻. The nitrile group in acetonitrile is not attacked by [Co^IPc]⁻.

The CoPc complexes were obtained in quantitative yields as organo-Co^{III}Pc (reaction *b*), or Co^{II}Pc (reaction *d*), or, after air-oxidation of the unchanged [Co^IPc]⁻, as Co^{II}Pc (non-occurrence of reactions *a* and *c*) in quantitative yield.

These results show that the cobalt(1)-phthalocyanine anion [Co^IPc] differs from cobal(1)amine^[2,6] and other strong nucleophiles by not undergoing nucleophilic additions; instead, as far as has been determined, it reacts only *via* nucleophilic substitution, with the exception of the reduction of nitro- and nitroso compounds. Thus [Co^IPc]⁻ resembles nucleophiles such as I⁻ in its selective behavior, but is considerably more reactive (relative logarithmic nucleophilic character of I⁻: $n = 7.42^{[7]}$; that of [Co^IPc]⁻ is $n = 10.8^{[5a]}$). [Co^IPc] is thus to be regarded as a very strong soft^[7] nucleophile (high polarizability of the 3d_{z²} orbital of Co^I) with low basicity.

The selectivity for substitution reactions together with the strong nucleophilicity, the low reduction potential (−0.37 V^[8]), and the extremely high stability recommend use of cobalt(1)-phthalocyanine anion, in spite of its high molecular weight (571), as a reagent for removal of β-halogenated alkyl protecting groups from sensitive systems^[3b,9] such as penicillin and cephalosporin derivatives^[3b].

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(1a), 123-72-8; (1b), 100-52-7; (1c), 140-88-5; (1d), 103-71-9; (1e), 124-38-9; (2a), 874-60-2; (2b), 93-97-0; (2c), 71616-09-6; (2d), 108-90-7; (3a), 108-95-2; (3b), 105-53-3; (4a), 98-95-3; (4b), 932-98-9; (4c), 75-05-8; [Co^IPc]⁻, 18974-06-6; *p*-CH₃ C₆H₄ CO Co^{III}Pc, 71616-28-9; C₆H₅CO Co^{III}Pc, 71616-29-0; Co^{III}Pc, 3317-67-7

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Isopropyl Carboxylates—A New Class of Insect Pheromones

By Wittko Francke, A. R. Levinson, T.-L. Jen, and H. Z. Levinson^[*]

The hide beetle *Dermestes maculatus* (Deg.), which feeds on animal tissues and animal products both as larva and as imago, causes considerable damage to stored products^[1]. We have identified the pheromone bouquet of this beetle as a basis for biotechnological pest control (see Table 1).

In an exocrine abdominal gland absent in females, sexually mature males produce a series of sex-specific volatile compounds showing high biological activity^[2]. GC-MS studies on pentane extracts^[3] of prepared glands were initially concerned with a group of four closely related substances. The most volatile component of this group ($M_r = 242$) has a molecular weight two units higher than that of the other three compounds, which are transformed into the first-mentioned one on catalytic hydrogenation.

The ions observed at $m/z = 102$ (14%) and 115 (11.5%) in the mass spectrum of this substance are typical products of a McLafferty rearrangement and, in conjunction with intense fragments at $M^+ - 41$ (22%) and $M^+ - 42$ (28.5%), indicate the propyl ester of a carboxylic acid with 12 carbon atoms^[4]. In fact, isopropyl laurate showed the same gas chromatographic retention time as the natural product and an identical mass spectrum.

Thus it had also been established that the other three components must be unbranched isopropyl dodecenoates. The principal component was isolated by preparative gas chro-

Table 1. Quantitative composition of the isopropyl ester pheromone bouquet of male hide beetle *Dermestes maculatus* (Deg.). The weights refer to an individual insect (total ca. 0.9 µg).

Carboxylic acid	Type	Weight [ng]
Lauric acid	C ₁₂	ca. 2.5
Z-5-Dodecenoic acid	Z-5-C ₁₂	300
Z-7-Dodecenoic acid	Z-7-C ₁₂	1
Lauroleic acid	Z-9-C ₁₂	ca. 0.1
Myristic acid	C ₁₄	25
Z-5-Tetradecenoic acid	Z-5-C ₁₄	50
Z-7-Tetradecenoic acid	Z-7-C ₁₄	100
Myristoleic acid	Z-9-C ₁₄	150
Palmitic acid	C ₁₆	25
Palmitoleic acid	Z-9-C ₁₆	200
Oleic acid	Z-9-C ₁₈	50

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matography^[5] and afforded heptanal as the major product on micro-ozonolysis; synthetic isopropyl Z-5-dodecenoate proved to be identical with the natural product. Identification of the other two compounds of mass 240 as isopropyl Z-7- and Z-9-dodecenoate was accomplished by comparison of their gas chromatographic retention times and mass spectra^[6] with those of authentic compounds prepared from the corresponding alkenols^[7] by oxidation and esterification (see Table 1).

The Kováts indices $I_{WG11, 150^\circ C}$ ^[8] of the isopropyl esters of all straight-chain dodecenoic acids are listed in Table 2: index differences of one unit can be distinguished on co-injection at comparable concentration; the working temperature must be reduced for smaller differences. It is seen that, on steady shift of the double bond from position 2 to 11, the initially more rapidly eluting Z compounds are "overtaken" by the E isomers. Isopropyl Z-6- and E-6-dodecenoate appear simultaneously; the ester of Z-5-dodecenoic acid is eluted faster than all other isopropyl dodecenoates.

Table 2. Kováts indices (*I*) of unbranched isopropyl dodecenoates on WG 11 at 150 °C [8].

Subst.	<i>I</i>	Subst.	<i>I</i>	Subst.	<i>I</i>	Subst.	<i>I</i>
Sat.	1841	E-5	1867	E-8	1876.5	11	1893
Z-5	1859	Z-6	1872	Z-3	1877	Z-9	1894
Z-4	1862	E-6	1872	E-9	1884.5	E-10	1906
Z-2	1864	E-7	1874	Z-8	1885	Z-10	1926
E-4	1866	Z-7	1876	E-3	1885.5	E-2	1970

Four other sex-specific substances found in the glands of male hide beetles contained two CH₂ groups more than the compounds previously identified. Gas chromatographic retention times and mass spectra^[6] were in agreement with synthetic samples of methyl myristate and isopropyl Z-5-, Z-7-, and Z-9-tetradecenoate.

In the same way the isopropyl esters of palmitic, palmitoleic, and oleic acids were also detected as male-specific components of the gland extract.

Table 1 shows a quantitative composition of this pheromone bouquet, which is the most extensive yet identified in beetles. A mixture of synthetic substances in the same ratio exhibited similar electro- and behavioral-physiological activities as did pentane extract of the abdominal glands of male hide beetles. The isopropyl carboxylates now found for the first time in insects thus constitute a new class of pheromones.

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