The syntheses of mono- and disubstituted phthalocyanines using a dithioimide

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This paper is dedicated to Professor John T. Edward

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Hydrolysis of 5-neopentoxy-1,3-diiminoisoindoline gave 5-neopentoxy-1*H*-isoindole-1,3(2*H*)-dione (4-neopentoxyphthalimide), which, on treatment with Lawesson's reagent, yielded the thiophthalimides, 5-neopentoxy-1*H*-isoindole-1,3(2*H*)-dithione, 2,3-dihydro-6-neopentoxy-3-thioxo-1*H*-isoindol-1-one, and 2,3-dihydro-5-neopentoxy-3-thioxo-1*H*-isoindol-1-one. Attempted S-alkylations of the thiophthalimides resulted in the formation of β-isoindigos and N-alkylation products. In a new phthalocyanine synthesis crossed condensations of 1,3-diiminoisoindoline with 5-neopentoxy-1*H*-isoindole-1,3(2*H*)-dithione yielded mixtures of phthalocyanines from which 2-neopentoxyphthalocyanine and 2,16-dineopentoxyphthalocyanine could be purified in part from other phthalocyanines.

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L'hydrolyse de la néopentoxy-5 diimino-1,3 indoline conduit à la néopentoxy-5 1*H*-isoindole (2*H*)-dione-1,3 (néopentoxy-4 phtalimide) qui, par traitement avec le réactif de Lawesson, fournit les thiophtalimides, néopentoxy-5 1*H*-isoindole (2*H*)-dithione-1,3, dihydro-2,3 néopentoxy-6 thioxo-3 1*H*-isoindolone-1 et dihydro-2,3 néopentoxy-5 thioxo-3 1*H*-isoindolone-1. Des essais de S-alkyler les thiophtalimides ont conduit à la formation de β-isoindigos et de produits de N-alkylation. Dans une nouvelle synthèse de la phtalocyanine, des condensations de la diimino-1,3 isoindoline avec la néopentoxy-5 1*H*-isoindole (2*H*-dithione-1,3 ont conduit à des mélanges de phtalocyanines à partir desquels on a pu purifier en partie la néopentoxy-2 phtalocyanine et la dinéopentoxy-2,16 phtalocyanine.

Although symmetrical tetra (1–3) and octasubstituted (4–6) phthalocyanines are well known, the synthesis of simple mono- (7), disubstituted (8), and other unsymmetrical phthalocyanines (9, 10) remains a difficult problem. A typical symmetrical phthalocyanine synthesis involves the self-condensation of 5-substituted or 4,5-disubstituted-1,3-diiminoisoindolines (4, 11). A simple strategy available to form unsymmetrical phthalocyanines is the mixed condensation of two different 1,3-diiminoisoindolines to obtain the desired mono-, di-, or trisubstituted phthalocyanines. In fact, condensation of 1,3-diiminoisoindoline (**1**) and 5-neopentoxy-1,3-diiminoisoindoline (**2**) does give mixtures of unsubstituted, mono-, di-, tri-, and tetraneopentoxyphthalocyanines (**3**–**8**) as expected when analyzed by mass spectroscopy.[2]

We envisioned that a completely new approach to phthalocyanine synthesis was required. If we could perform a crossed condensation of substrates in which one of the substrates is unable to self-condense and if we could lower the temperature of phthalocyanine formation so that crossed condensation is favoured over self-condensation of the other substrate, then specifically substituted phthalocyanines could be formed as shown in Scheme 1.

Although phthalic anhydrides self-condense, probably via phthalimides to form phthalocyanines in the presence of urea (12) at very high temperatures, phthalimides are inert to self-condensation under 150°C. On the other hand, 1,3-diiminoisoindoline (**1**) and its derivatives readily form phthalocyanines at 150°C but only slowly below 100°C unless special catalytic bases are used (13). We believed that if we used thiophthalimides in crossed condensation reactions, then the nucleophilic addition of the 1,3-diiminoisoindoline (**1**) to a dithiophthalimide such as 1*H*-isoindole-1,3(2*H*)-dithione (**9**) or 5-neopentoxy-1*H*-isoindole-1,3(2*H*)-dithione (**10**) would in fact be much faster than self-condensation of **1**, as the high reactivity of the thiocarbonyl group is well known (14). It is thus possible that a crossed condensation of **1** and **10** could occur even at ambient temperature to form exclusively the desired 2,16-dineopentoxyphthalocyanine (**5**) (along with 2,17-dineopentoxyphthalocyanine), but no other compounds. In addition, any self-condensation of **1** would yield the highly insoluble unsubstituted phthalocyanine (**3**), which may then be separable from the organic solvent-soluble **5**. Another attractive feature of this strategy is the fact that only **5** (the "*para*" disubstituted isomer) would be formed and not 2,9-dineopentoxyphthalocyanine (**6**) (the "*ortho*" disubstituted isomer).

The first step in the realization of the strategy outlined in Scheme 1 is the preparation of the required thiophthalimide. Thus treatment of 4-nitrophthalimide (**11**) with neopentoxides led only to the recovery of **11**, and no 4-neopentoxyphthalimide (**12**) was formed (Scheme 2). Indeed, the preparations of 4-alkoxyphthalimides are known in the literature (15) but only through a lengthy 5-step synthesis from diethyl 4-nitrophthalate. Since it is known that 1,3-diiminoisoindolines can be hydrolyzed to phthalimides (16) and since we readily had available 5-neopentoxy-1,3-diiminoisoindoline (**2**) from previous studies on binuclear phthalocyanines (17), **2** was converted to 4-neopentoxyphthalimide (**12**) by refluxing **2** in aqueous dioxane (Scheme 2). Treatment of **12** with excess 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (**13**) (Lawesson's reagent) (18) gave 5-neopentoxy-1*H*-isoindole-1,3(2*H*)-dithione (**10**) in 82% yield while the reaction of **12** with only 0.5 equivalents of **13** gave **10**, admixed with the two possible monothionated products, 2,3-dihydro-6-neopentoxy-3-thioxo-1*H*-isoindol-1-one (**14**) and 2,3-dihydro-5-neopentoxy-3-thioxo-1*H*-isoindol-1-one (**15**) in 37, 16, and 24% yields respectively. The new thiophthalimides **10**, **14**, and **15** were fully characterized by elemental analysis and spectroscopic data and compared with the known **9** and monothiophthalimide by uv–vis (Table 1) (19) and ^{13}C nmr (Table 2) (20) spectroscopy.

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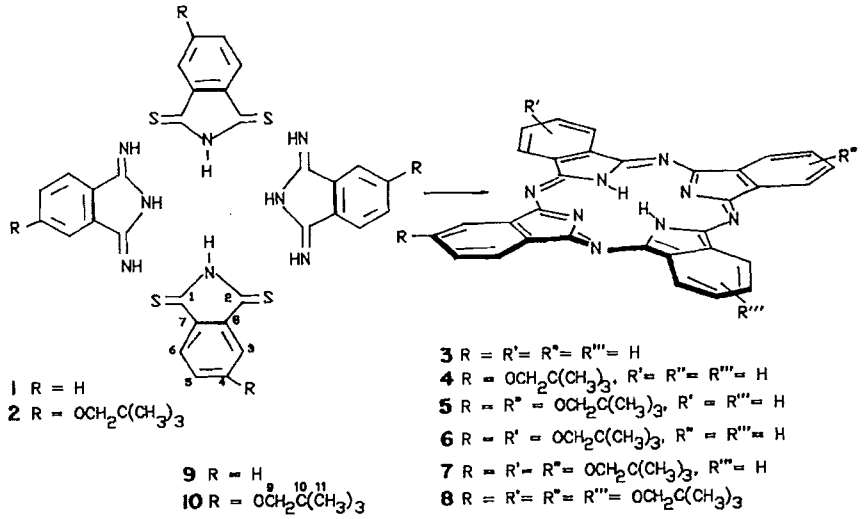
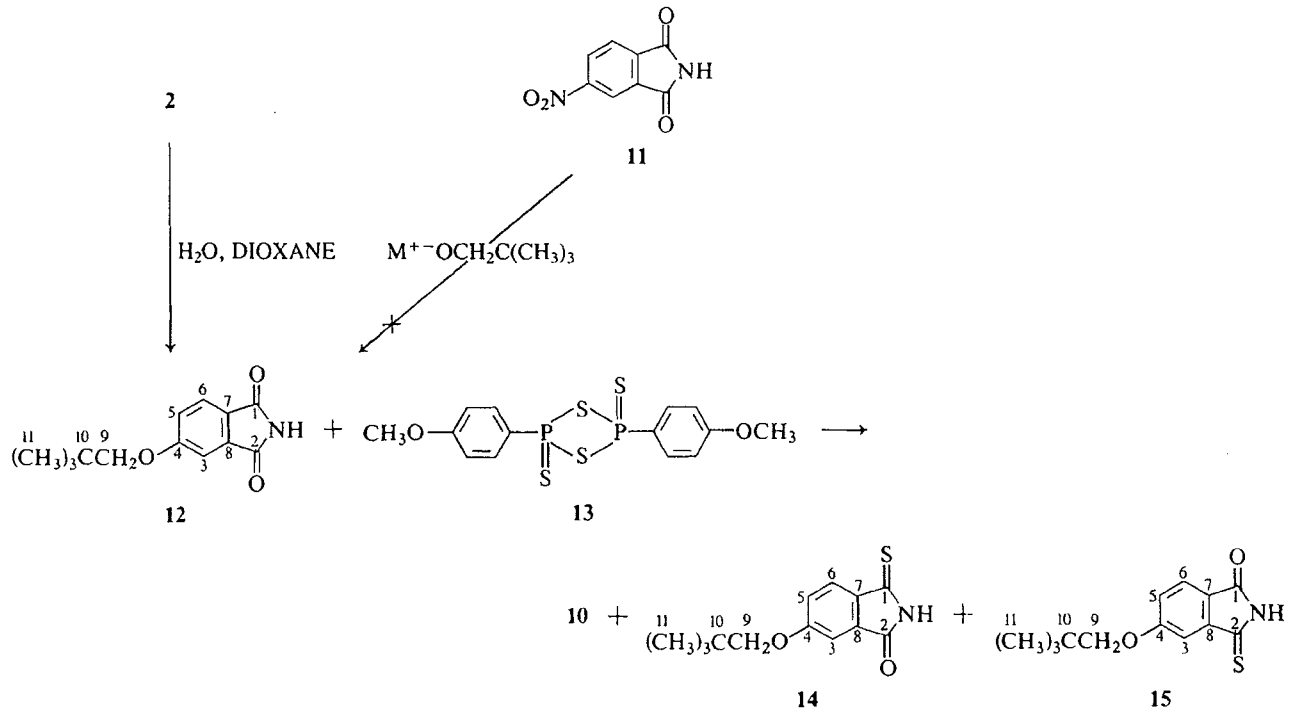
[2]S. Greenberg and C. C. Leznoff, unpublished results.



SCHEME 1



SCHEME 2

In previous studies (17) we had shown that **2** readily self-condenses to 2,9,16,23-tetraneopentoxyphthalocyanine (**8**) at 150°C in 2-*N*,*N*-dimethylaminoethanol. Control studies conducted to determine the maximum temperature at which **1** will not exhibit phthalocyanine formation showed that **1** was stable in 2-*N*,*N*-dimethylaminoethanol at 70°C or below and only reacted slowly below 95°C. Thus, **1** was dissolved in 2-*N*,*N*-dimethylaminoethanol at 50°C and **10** was added to this mixture and stirred at 80–90°C for 24 h to give, after precipitation with water, a dark-coloured residue containing phthalocyanines (Experiment 1) (Scheme 1). Extraction of the residue with methanol removed most non-phthalocyanine impurities. Thus the formation of phthalocyanines by the crossed condensation of a dithiophthalimide with a 1,3-diiminoisoindoline has been demonstrated for the first time. Further extraction of the residue with tetrahydrofuran (THF) (first phthalocyanine extract) yielded a solution of phthalocyanines that contained a mixture of **3**–**8** as revealed by mass spectroscopy (Table 3). The mixture contained 2,16-dineopentoxyphthalocyanine (**5**) (and possibly the 2,9-dineopentoxyphthalocyanine isomer (**6**)) as desired but significant quantities of phthalocyanine (**3**), 2-neopentoxyphthalocyanine (**4**), and 2,9,16-trineopentoxyphthalocyanine (**7**) were also produced, while 2,9,16,23-tetraneopentoxyphthalocyanine (**8**) was formed in traces only. Of course, the relative ratio of the parent ions of **3**–**8** is not necessarily an accurate representation of the relative abundances of **3**–**8**, but it does give us a strong indication that the exclusive formation of **5** did not occur. As phthalocyanines give strong parent ions in their mass spectra (21) and pure **8** does not give fragment ions corresponding to **3**–**7** (17), we can be confident that the

TABLE 1. Absorption spectra of phthalimides, thiophthalimides, and β-isoindigos in $CHCl_3$ at 24°C

Compound	λ_{max}(nm) (ε log)	Reference
Phthalimide[a]	240 (3.28), 296 (3.32)	19
Thiophthalimide[a]	244 (3.71), 298 (4.15), 334 (4.05)	25[b]
9[a]	246 (4.05), 264 (3.83), 376 (4.36)	25
10	282 (4.25), 292 (4.15), 380 (4.40)	
12	248 (4.23), 282 (3.32), 326 (3.54)	
14	256 (4.22), 304 (4.18), 344 (4.09), 366 (4.04)	
15	256 (4.38), 306 (4.17), 370 (3.54)	
16	248 (4.14), 362 (4.30), 390 (4.22)	
17	256 (4.59), 336 (4.25), 421 (4.71), 442 (4.84), 464 (4.79)	36[b]
18	246 (4.00), 356 (4.06), 394 (3.92)	
19	256 (4.09), 336 (3.75), 424 (4.22), 444 (4.37), 468 (4.30)	36[b]
22	246 (4.12), 320 (3.84), 420 (4.23), 440 (4.43), 466 (4.23)	

[a]The absorption spectra of these known compounds were recorded for comparison with the other unknown compounds.
[b]The spectra of closely related compounds are described.

TABLE 2. ^{13}C nuclear magnetic resonance chemical shifts in ppm (δ) of some phthalimides and thiophthalimides

	Carbon[a]										
Compound	1	2	3	4	5	6	7	8	9	10	11
Phthalimide[b]	167.60	167.60	123.50	134.10	134.10	123.50	132.50	132.50	—	—	—
Thiophthalimide[b]	170.06	197.01	123.01	133.69	134.30	123.92	127.92	137.33	—	—	—
9	197.32	197.32	123.10	133.56	133.56	123.10	135.08	135.08	—	—	—
10	196.68[c]	197.27[c]	107.01	164.52	120.76	125.03	128.38	137.48	78.76	31.91	26.49
12	168.57	168.57	108.46	164.69	120.52	125.09	124.18	135.18	78.65	31.77	26.36
14	196.76	170.05	107.38	164.46	120.97	125.80	130.40[c]	130.46[c]	78.85	31.89	26.45
15	170.18	197.24	108.70	164.76	120.25	124.71	119.71	139.76	78.63	31.85	26.44
16[d]	197.46	197.46	123.03	132.95	132.95	123.03	134.76	134.76	—	—	—

[a]The numbering of the carbon atoms in the listed compounds follows that given for these structures in the schemes and does not follow from the names of the compounds.
[b]The ^{13}C nmr spectra of these and related known compounds (20) were recorded and used to help assign the chemical shifts of the other unknown compounds.
[c]These values may be interchanged.
[d]The chemical shift of the N-methyl group is 31.04 ppm. In comparison, the chemical shift of the S-methyl group of **17** is 13.49 ppm.

ions observed are parent ions due to **3**–**8** and not fragment ions corresponding to **3**–**7**. Further extraction of the crude residue with toluene and, finally, with more tetrahydrofuran gave, again by mass spectroscopic analysis (Table 3), smaller quantities of phthalocyanines but fractions richer in the mono- and unsubstituted phthalocyanines **4** and **3** respectively. From previous work in our laboratory (9) we knew that mixtures of substituted mononuclear phthalocyanines are almost impossible to separate by flash chromatography (22) or even preparative thin-layer chromatography (tlc), probably because of aggregation phenomena. Since we had some phthalocyanine extracts that were already partially rich in **5** and **4**, we felt that vacuum liquid chromatography (vlc) (23), a very powerful separation technique, may give us pure samples of **5** and **4**. Thus further efforts to purify the first extract by vlc were attempted. Although it appeared that several blue-green bands readily separated on the column, again mass spectroscopic examination of each band (Table 3) showed that substantial contamination of each fraction remained. Some fractions obtained by vlc were rich in 2,16-dineopentoxyphthalocyanine (**5**) and one fraction contained almost pure 2-neopentoxyphthalocyanine (**4**) (with a trace of **5**) (Table 3), again by mass spectroscopic analysis of each chromatographic fraction. It should be noted that our previously reported (9) synthesis of an unsymmetrical phthalocyanine was based on a polymer support method yielding only the desired product, and no exhaustive chromatography was necessary to isolate the desired product. In addition mass spectroscopy revealed the presence of the desired product only. As a word of caution, other workers have recently reported the preparation of a mononitrophthalocyanine (7), a dicarboxyphthalocyanine (8), and an unsymmetrical octasubstituted phthalocyanine (10). Although the products were purified by flash chromatography in some cases (10) and the compounds gave sometimes acceptable elemental analysis (7, 10), no mass spectral data were recorded in detail (7, 8, 10) and in these instances mixtures of phthalocyanines may have been obtained. For example, an elemental analysis of a disubstituted phthalocyanine could be identical to that of a mixture of unsubstituted, mono-, di-, tri-, and tetrasubstituted phthalocyanines, especially since a mixture of this type usually shows up as one spot on tlc examination.[2]

In another experiment (Table 3, Experiment 2), we tried to optimize the formation of 2-neopentoxyphthalocyanine (**4**) by partially self-condensing an excess of **1** at 120°C and then adding a minimal quantity of **10** in a crossed phthalocyanine condensation (Scheme 1). The dark residue, obtained after the

TABLE 3. Mass spectroscopic data on the mixtures of phthalocyanines **3–8** in crossed condensation reactions of **1** and **10**

Experiment	Extract No.[a]	Fraction (vlc)	Mass spectrum[b] *m/z* (relative intensity %)
1	1	[c]	858(1), 772(22), 686(100), 600(45), 514(15)
1	1	2	858(5), 772(41), 686(10)
1	1	4	858(1), 772(87), 686(100), 600(11)
1	1	5	772(4), 686(100), 600(17)
1	1	6	772(7), 686(100), 600(6)
1	1	9	686(12), 600(100), 514(100)
1	2	[c]	772(1), 686(54), 600(100), 514(32)
1	2	1a[d]	772(3), 686(100)
1	2	1b[d]	686(100), 600(27)
1	2	1c[d]	686(84), 600(100)
1	2	2	686(16), 600(100)
1	2	3	686(8), 600(100)
1	2	3[e]	686(1), 600(100)
1	3[f]	—	686(18), 600(92), 514(100)
1	3[g]	—	686(1), 600(66), 514(100)
1	R[h]	—	600(29), 514(100)
2	1	—	772(1), 686(26), 600(80), 514(100)
2	2	—	772(1), 686(41), 600(100), 514(72)
2	3*f*	—	686(48), 600(100),
2	3[g]	—	686(1), 600(35), 514(100)
2	R[h]	—	600(12), 514(100)

[a]Extractions of phthalocyanines were performed as follows; extract 1 with THF for 5 h, extract 2 with THF for 19 h (In Expt. 1 a prior extraction with toluene for 10 h was performed), extract 3 with THF for 48 h.

[b]The peaks at 514, 600, 686, 772, and 858 are assigned as the parent peaks of **3**, **4**, **5** + **6**, **7**, and **8** respectively.

[c]Before further purification.

[d]Further flash chromatography of vlc fraction 1 gave fractions 1a, 1b, and 1c, which were analyzed by mass spectroscopy.

[e]This fraction is the same as the above entry (vlc fraction 3) but has been recrystallized.

[f]This sample is the evaporated filtrate.

[g]This sample is a precipitate formed before evaporation of the filtrate.

[h]Unextracted residue.

reaction, was purified as before to give a blue phthalocyanine solid. Extraction with THF for 5, 19, and 48 h gave extracts 1–3 respectively. From extract 3 a blue product precipitated. Mass spectroscopic analysis (Table 3) of extracts 1, 2, 3 (precipitate) and 3 (filtrate) and the remaining residue again showed that extracts 1 and 2 contained varying amounts of **3–7**, extracts 3 (precipitate) contained mostly **3** and **4**, while extract 3 (filtrate) contained mostly **4** and **5**. The solid blue residue contained mostly **3**. Further purifications by vlc on these extracts were not attempted.

Although we had succeeded in developing a new phthalocyanine synthesis at moderate temperatures based on thioimides, the yields of phthalocyanines in the key crossed condensation steps were low and the desired selectivity leading to mono- or disubstituted phthalocyanines was at best only partially achieved. Since 1-alkoxy-3-iminoisoindolines have been implicated as intermediates in phthalocyanine formation (24), we believed that 1-thioalkoxy-3-thioisoindolines could be used as a reactive partner instead of dithiophthalimides in phthalocyanine synthesis. Alkylation of thioamide-type compounds has been accomplished in many studies (25–29) giving exclusive S-alkylation as opposed to N-alkylation. In a model study of alkylations on dithiophthalimide (**9**) by a wide variety of methods encompassing basic (25–27), Lewis acid (27, 28), or neutral (29) conditions (Table 4), only N-alkylation or the formation of dialkyldithio-β-isoindigos took place (Scheme 3, Tables 1, 2, and 4). Thus methylation (25) of **9** with dimethyl sulfate and base gave *N*-methyldithiophthalimide (**16**) in 25–63% yield but the use of iodomethane and base (26, 27) gave mostly *S,S'*-dimethyldithio-β-isoindigo (**17**) (30) in 12–60% yield (Table 4). Another method using **9** and triethylorthoformate (29) at 180°C gave *N*-ethyldithiophthalimide (**18**) and *S,S'*-diethyldithio-β-isoindigo (**19**) (30), but again no simple S-alkylation occurred (Table 4). Still other alkylation methods (27, 28) exhibited no reaction or gave intractable products (Table 4).

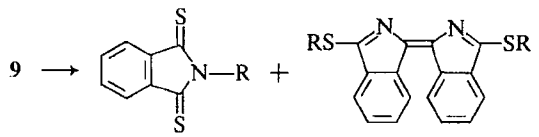
Since the desired S-alkylated dithiophthalimide could not be prepared and since 3-ethoxyisoindol-1-one (**20**) was known (31), then simple treatment of **20** with Lawesson's reagent (**13**) (18) should yield 3-ethoxyisoindol-1-thione (**21**), which could be used in a cross-condensation reaction with **1**. Treatment of **20** with **13** did not give the desired **21**, but an unstable red compound **22**, which we tentatively assign by spectroscopic data (Tables 1 and 2) to 3-(3-ethoxy-1*H*-isoindol-1-ylidene)-2,3-dihydro-1*H*-isoindol-1-thione (**22**) as shown in Scheme 4. This last experiment indicates to us that the use of thiocarbonyl compounds in phthalocyanine synthesis is invariably complicated by the concomitant formation of isoindigos.

There have only been a few studies on the mechanism of phthalocyanine formation from phthalonitriles (32) or via amine–imidine condensations (24, 33). The formation of phthalocyanines **4–8** from condensation of **1** and the dithione **10** must obviously result from the displacement and hence removal of

TABLE 4. Alkylation reactions of dithiophthalimide (**9**) under different conditions

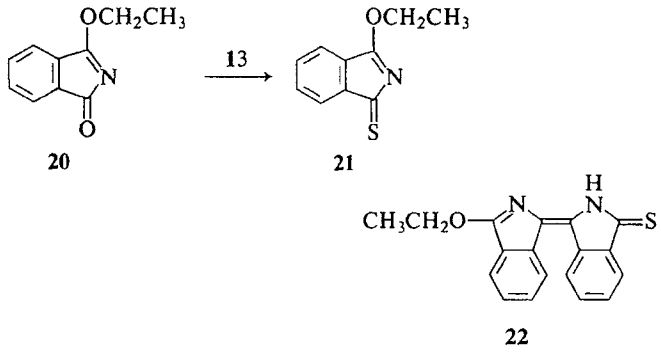
Alkylating agent	Base	Solvent	Temperature (°C)	Time (h)	Products (% yield)	Reference[a]
$(CH_3O)_2SO_2$	2 *M* NaOH	EtOH	0	0.17	**16** (25)	25
$(CH_3O)_2SO_2$	Et_3N	Toluene–THF	22	20	**16** (63)	
CH_3I	—	Dioxane	110	20	**9**	
$(CH_3O)_2SO_2$	—	Toluene	110	20	dec.[b]	
CH_3I	—	Acetone	22	20	**9**	
$(CH_3)_3\overset{+}{O}BF_4^-$	—	CH_2Cl_2	22	20	**17** (16)	28
CH_3I	0.8 *M* NaOH	MeOH	22	18	**17** (60)	27
$BF_3 \cdot OEt_2$	—	Toluene	120	2	**9**	27
$BF_3 \cdot OMe_2$	—	Toluene	60[c]	18	dec.[b]	27
CH_3I	$(Bu)_4NOH$	THF	22	18	**16** (22)[d]	
CH_3I	1 *M* CsOH	MeOH	22	18	**17** (12)	
CH_3I	1 *M* CsOH	MeOH	−20	5	**9**	
$HC(OEt)_3$	—	$HC(OEt)_3$	90	60	**9**	29
$HC(OEt)_3$	—	$HC(OEt)_3$	180	5	**18** (13)[e]	29

[a]The references refer to published methods of achieving S-alkylation.
[b]Decomposition of the starting material to an unresolvable mixture of compounds has occurred.
[c]At 22°C only **9** was recovered.
[d]Some **17** and other spots were detected on tlc.
[e]In addition **19** (8) was isolated.



16 R = CH_3 **17** R = CH_3
18 R = C_2H_5 **19** R = C_2H_5

SCHEME 3



20 **21** **22**

SCHEME 4

the thione functional groups by ammonia, amines, or imines. The original hypothesis assumed that condensation of **1** and **10** would give in the first step an intermediate trimeric species (**23**) (Scheme 5), which on reaction with a 2nd equivalent of **10** would lead to **5**. Indeed, the lower temperature at which phthalocyanine formation is initiated (as low as 20°C) indicates that this first step is a likely possibility. It could happen, however, that although we have lowered the *initiation* step of phthalocyanine formation, the *propagation* step can still proceed rapidly at these modest temperatures. Thus intermediate **23** may react with more **10** giving 2,16-dineopentoxyphthalocyanine (**5**), but it could also react with more **1** giving the monosubstituted 2-neopentoxyphthalocyanine (**4**). In addition, **23** may undergo a N–H tautomeric shift giving the trimeric intermediate **24**. Trimeric intermediate **24** could react with **1** in two ways, giving two dimeric intermediates **25** and **26**, the former possessing a neopentoxy substituent. A N–H tautomeric shift of **25** could give a different dimeric intermediate **27**. The unsubstituted dimeric intermediate **26** could self-condense or react with **1** or **27** to give the phthalocyanine (**3**) or more **4**. The substituted dimeric intermediate **27** could react with **1** or **26** to give **2** or more **4** and with itself to give **5** and 2,9-dineopentoxyphthalocyanine (**6**). The generation of the monomeric 5-neopentoxy-1,3-diiminoisoindoline (**2**) in this reaction opens the door to other pathways of phthalocyanine formation. Thus **2** could react with **25** to generate 2,9,16-trineopentoxyphthalocyanine (**7**), or to form a new dimeric intermediate **28** containing two neopentoxy substituents. Intermediate **28** can further self-condense or react with **2** to give 2,9,16,23-tetraneopentoxyphthalocyanine (**8**). Alternatively **28** can condense with **26** to give **6** directly. Further condensation of **28** with **1** or **26** could give a new trimeric intermediate **29**, containing two neopentoxy substituents. Condensation of **29** with **2**, **10**, or even **25** could give more **7**, while condensation with **1**, **26**, or **27** could give **6**. Although Sato *et al.* (34) have shown that elemental sulfur (perhaps as thiolate anions) can act as a catalyst in the formation of 1,3-diiminoisoindolines from phthalonitriles, there was no report that phthalocyanine formation occurred under their conditions. We did notice in our reactions of **1** with **10** that a small amount of elemental sulfur was produced and this sulfur could account for the catalytic self-condensation of **1** to **3**. Indeed, control experiments conducted on **1** and elemental sulfur showed phthalocyanine formation starting at 50°C.[2] Elemental sulfur could not account directly for the formation of **4**–**8** but could further catalyze the reactions outlined in Scheme 5. Another complication not outlined in Scheme 5 is the possible production of ammonia gas, which could form **2** directly from **10**. The fact that the condensations of **1** and **10** are conducted under a steady stream of argon somewhat vitiates against this possibility. A full description of phthalocyanine formation is still clouded by the multiplicity of

possible intermediates and catalysis by intermediates and by-products.

In this paper we have demonstrated that phthalocyanine formation readily occurs at modest temperatures from a 1,3-diiminoisoindoline and a dithiophthalimide, but that selective formation of mono- or disubstituted phthalocyanines was only partially achieved.

Experimental

Matheson high-purity argon was used to maintain inert atmosphere conditions. Infrared (ir) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs for solids or as neat films between NaCl discs. Nuclear magnetic resonance (nmr) spectra for carbons and protons were recorded on a Bruker AM300 nmr spectrometer using deuterochloroform as solvent and tetramethylsilane as the internal standard unless otherwise stated. The positions of the signals are reported in δ units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).)

The visible–ultraviolet spectra (uv) were recorded on a Hewlett Packard HP8451A Diode Array spectrophotometer. Mass spectra (ms) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode.

Melting points (mp) were determined using a Kofler hot stage melting point apparatus and are uncorrected. Thin-layer chromatography (tlc) was performed using silica gel G as the adsorbent. Flash chromatography was performed using silica gel of particle size 20–45 μm. All reactions were stirred with a magnetic stirrer. All solvents were freshly distilled before use. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont.

4-Neopentoxyphthalimide (12)

A suspension of 5-neopentoxydiiminoisoindoline (**2**) derived from 134 mg (0.63 mmol) of 4-neopentoxyphthalonitrile in 3 mL of a 1:1 mixture of water–dioxane was refluxed for 22 h. Since the crude diiminoisoindoline contained sodium methoxide (from the method of preparation), 28 mg of ammonium chloride (0.52 mmol) was added to the mixture. During the first 2–3 h ammonia was evolved and the suspension turned clear, and later a precipitate was formed. After cooling to room temperature the crude product was diluted with ethyl acetate and the organic layer was washed thoroughly with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to a small volume. The crude product was purified using silica gel column chromatography and elution with ethyl acetate – petroleum ether (1:4). The product was recrystallized from a mixture of ethyl acetate – hexanes to give, in 75% yield, 110 mg of 5-neopentoxyphthalimide (**12**) as white crystals, mp 170–171°C (with previous darkening at 151–153°C); ir (cm^{-1}): 3240 (NH), 1780 (CO), 1740 (CO), 1630, 1370, 1240, 1020, 760; ^1H nmr δ: 7.75 (d, J = 8.3, 1H), 7.73 (br, 1H, NH), 7.32 (d, J = 2.2, 1H), 7.20 (dd, J = 8.3, 2.2, 1H), 3.75 (s, 2H, CH_2O), 1.07 (s, 9H, $(CH_3)_3C$); ms m/z: 233 (M^+, 10), 218 ($M^+ - 15$, 2.5), 175 (11), 164 (12), 71 (65), 43 (100). *Anal.* calcd. for $C_{13}H_{15}NO_3$: C 66.94, H 6.48, N 6.00; found: C 66.84, H 6.64, N 5.96.

5-Neopentoxy-1H-isoindole-1,3(2H)-dithione (10), 2,3-dihydro-6-neopentoxy-3-thioxo-1H-isoindol-1-one (14), and 2,3-dihydro-5-neopentoxy-3-thioxo-1H-isoindol-1-one (15)

A suspension of 192 mg (0.83 mmol) of **12** and 177 mg (0.44 mmol) of Lawesson's reagent (**13**) (18) in 2 mL of dry toluene was stirred at 90°C for 2.5 h. The reaction was followed by tlc (eluant toluene) and was stopped after 2.5 h, due to the formation of blue material at the base line when examined by tlc, even though not all of the starting material had reacted. After cooling to room temperature the crude product was purified by flash chromatography (22) using toluene as eluant. The first dark moving band gave, in 37% yield, 80 mg of 5-neopentoxy-1*H*-isoindole-1,3(2*H*)-dithione (**10**) as dark red-brown needles, mp 194–196°C (with previous softening); ir (cm^{-1}): 3260 (NH), 1625, 1480, 1450, 1350, 1230, 1120, 930, 840; ^1H nmr δ: 9.95 (br, 1H, NH), 7.78 (d, J = 8.4, 1H), 7.26 (d, J = 2.1, 1H), 7.20 (dd, J = 8.4, 2.1, 1H), 3.75 (s, 2H, CH_2O), 1.07 (s, 9H, $(CH_3)_3C$); ms m/z: 265 (M^+, 90), 250 ($M^+ - 15$, 10), 195 (93), 162 (60), 71 (45), 43 (100). *Anal.* calcd. for $C_{13}H_{15}NOS_2$: C 58.83, H 5.70, N 5.28; found: C 58.89, H 5.89, N 5.30.

Continued elution with toluene gave a yellow moving band. After evaporation of the solvent 2,3-dihydro-6-neopentoxy-3-thioxo-1*H*-isoindol-1-one (**14**) was isolated in 16% yield (33.5 mg) as orange crystals, mp 159–160°C; ir (cm^{-1}): 3240 (NH), 1745 (C=O), 1610, 1310, 1250, 1110, 830; ^1H nmr δ: 9.08 (br, 1H, NH), 7.86 (d, J = 8.4, 1H), 7.23 (d, J = 2.1, 1H), 7.18 (dd, J = 8.4, 2.1, 1H), 3.72 (s, 2H, CH_2O), 1.07 (s, 9H, $(CH_3)_3C$); ms m/z: 249 (M^+, 44), 179 (71), 71 (44), 43 (100). *Anal.* calcd. for $C_{13}H_{15}NO_2S$: C 62.62, H 6.07, N 5.62; found: C 62.77, H 6.00, N 5.79.

Continued elution with toluene gave a pink moving band. After evaporation of the solvent, 2,3-dihydro-5-neopentoxy-3-thioxo-1*H*-isoindol-1-one (**15**) was isolated in 23% yield (48.4 mg) as pink crystals, mp 139–142°C; ir (cm^{-1}): 3260 (NH), 1745 (C=O), 1605, 1490, 1310, 1085, 860, 775, 700; ^1H nmr δ: 9.45 (br, 1H, NH), 7.69 (d, J = 8.3, 1H), 7.40 (d, J = 2.1, 1H), 7.18 (dd, J = 8.3, 2.1, 1H), 3.74 (s, 2H, CH_2O), 1.07 (s, 9H, $(CH_3)_3C$); ms m/z: 249 (45), 179 (57), 71 (53), 43 (100). *Anal.* calcd. for $C_{13}H_{15}NO_2S$: C 62.62, H 6.07, N 5.62; found: C 62.40, H 5.99, N 5.84.

Some unreacted **12** was not recovered.

N-*Methyldithiophthalimide (16)*

A solution of 110 mg of dithiophthalimide (**9**) (0.61 mmol) in 1 mL of 95% ethanol and 0.3 mL of 2 *M* sodium hydroxide (0.6 mmol) was diluted with 1 mL water and cooled to 0°C according to the procedure of Baguley and Elvidge (25). The red solution was stirred while 0.15 mL of dimethylsulfate was added dropwise during 2–5 min. After a further 5 min the solution was diluted with 2 mL water. The crude product was extracted with ether and the organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated to give 157 mg of crude product. The crude product was chromatographed using normal grade silica gel. Elution with toluene gave, in 25% yield, 30 mg of pure dark needles, mp 103–104°C (lit. (35) mp 98–100°C, 91–92°C); ir (cm^{-1}): 1460, 1410, 1355, 1330–1310, 1050, 960, 760, 750, 650; ^1H nmr δ: 7.78 (dd, J = 8.6, 2.5, 2H), 7.60 (dd, J = 8.6, 2.5, 2H), 3.77 (s, 3H, N-CH_3); ms m/z: 193 (M^+, 100), 117 ($M^+ - CS_2$, 28).

S,S-*Dimethyldithio-β-isoindigo (17)*

To a solution of 207 mg of **9** (1.16 mmol) in 3 mL of 0.8 *M* sodium hydroxide and 1 mL methanol, 0.06 mL of methyl iodide was added (0.96 mmol). The red solution became less intense in color and after a while a precipitate was formed. The suspension was stirred at room temperature for 18 h during which a red precipitate of *S,S*-dimethyldithio-β-isoindigo (**17**) appeared and the solution became clear. The methanol was evaporated under reduced pressure, water was added, and the insoluble material was filtered and washed with water. The crude product was dissolved in hot ethyl acetate and the hot suspension was filtered to remove 20 mg of insoluble material, which by mass spectra and ^1H nmr was shown to have a structure corresponding to an isoindigo trimer. This fraction was not further characterized. The crude **17** was recrystallized from ethyl acetate to give, in 60% yield, 92.8 mg of pure **17** as red or golden needles according to the concentration of the crystallizing solution, mp 260–263°C (lit. (30) mp 258°C); ir (cm^{-1}): 1470, 1455, 1340, 1265, 1030, 755, 660; ^1H nmr δ: 8.79 (d, J = 7.5, 2H), 7.60–7.40 (m, 6H), 2.95 (s, 6H, SCH_3); ^{13}C nmr δ: 172.70, 145.56, 139.80, 137.82, 129.22, 128.16, 126.56, 119.81, 13.49; ms m/z: 322 (M^+, 100), 307 ($M^+ - 15$, 80), 274 ($M^+ - SCH_3$, 73), 161 (M^{+2}, 10), 146 ($M - 15$, 25).

The fine structure of **17** regarding geometrical isomerism is not clear. Elvidge and Golden (36) suggested the *trans* form for dialkylimino-β-isoindigos since these compounds did not form complexes with metals. Dithio-β-isoindigo, on the other hand, did form metal complexes and was suggested by Drew and Kelly (30) to be in the *cis* form.

N-*Ethyldithiophthalimide (18) and* S,S-*diethyldithio-β-isoindigo (19)*

A solution of 125 mg of dithiophthalimide (**9**) (0.70 mmol) and

10 mL of triethylorthoformate was heated to 160°C for 3 h and then to 180°C according to the procedure of Rutavichyus and Iokubaitite (29). The volatile material (5–7 mL) had been removed by distillation through a fractionating column at 180°C. The solution was cooled and the excess triethylorthoformate was removed under pressure at 60°C/0.1 Torr (1 Torr = 133.3 Pa). Preliminary purification of the crude reaction mixture was done by column chromatography using normal grade silica gel. Elution with ether – petroleum ether (1:9) gave some elemental sulfur and 18.3 mg of *N*-ethyldithiophthalimide **18** (13% yield) as red needles, mp 51–53°C (lit. (35) mp 47–48°C, 81–83°C); ir (cm^{-1}): 1465, 1355, 1065, 765, 720, 700; ^1H nmr δ: 7.85 (dd, J = 8.7, 2.5, 2H), 7.66 (dd, J = 8.7, 2.5, 2H), 4.50 (q, J = 7, 2H, N-CH_2), 1.29 (t, J = 7, 3H, CH_2CH_3), ms m/z: 207 (M^+, 100), 191 (29), 179 (31).

Further elution of the silica gel gave 88 mg of a mixture consisting of *N*-ethyldithiophthalimide **18**, *S,S*-diethyldithio-β-isoindigo, **19**, and unreacted starting material, **9**. This mixture was further purified by preparative tlc using ether – petroleum ether (1:9) as eluting solvent. The yellow moving band consisting of **19** was extracted with ether in a Soxhlet apparatus to give, after solvent evaporation, 10 mg of pure **19** as golden needles in 8% yield, mp 126–128°C (with previous softening) (lit. (30) mp 162°C); ir (cm^{-1})): 1470, 1450, 1330, 1270, 1245, 1020, 745, 650; ^1H nmr δ: 8.78 (d, J = 7.3, 2H), 7.67–7.40 (m, 6H), 3.57 (q, J = 7.4, 4H, S-CH_2), 1.62 (t, J = 7.4, 6H, CH_2CH_3); ms m/z: 350 (M^+, 80), 321 (M^+ − 29, 100).

The unreacted dithiophthalimide was not recovered.

3-(3-Ethoxy-1H-isoindol-1-ylidene)-2,3-dihydro-1H-isoindol-1-thione (22)

A suspension of 1.08 g (6.09 mmol) of 3-ethoxy-isoindol-1-one (**20**) (31) and 1.36 g (3.36 mmol) of Lawesson's reagent (**13**) (18) in 10 mL of dry toluene was refluxed under argon for 2 h. After cooling to room temperature the crude product was purified by flash chromatography using toluene as eluant to give, in 12% yield, 111 mg of **22** as red crystals, mp >300°C; ir (cm^{-1}): 1635, 1530, 1340, 1140, 1080, 750; ^1H nmr (acetone-d_6) δ: 8.97 (d, J = 7.7, 1H), 8.63 (d, J = 7.8, 1H), 8.02 (d, J = 7.7, 1H), 7.78–7.54 (m, 5H), 4.79 (q, J = 7.0, 2H, CH_2O), 1.57 (t, J = 7.0, CH_3CH_2); ^{13}C nmr (DMSO-d_6) δ: 190.88, 170.66, 137.04, 136.03, 135.28, 132.73, 132.13, 131.64, 130.34, 129.75, 129.66, 128.41, 126.80, 124.44, 123.73, 120.56, 65.30, 14.38; ms m/z: 306 (M^+, 100), 277 (M^+ − 29, 87).

A synthesis of 2-neopentoxyphthalocyanine (4) and 2,16-dineopentoxyphthalocyanine (5) (Experiment 1)

The crude 1,3-diiminoisoindoline derived from 200 mg of phthalonitrile (1.56 mmol) in 2 mL of *N,N*-dimethylaminoethanol was heated to 50°C until completely dissolved. After 1 h, 274 mg of **10** (1.03 mmol) was added. The very light green solution turned red and then dark. The solution was stirred at 80–90°C under an argon atmosphere for 24 h. The mixture was cooled to room temperature, diluted with water, filtered, and washed thoroughly with water and then with methanol until the filtrate was almost clear. The crude product (112 mg) was extracted with methanol in a Soxhlet extractor for 10 h until the extract was almost clear. This process removed brown impurities. The desired product was then extracted for 5 h (extract 1) with freshly distilled THF to give 42 mg of a mixture of phthalocyanines. Mass spectra (Table 3) of the mixture showed that it consisted of mainly the 2,16-dineopentoxyphthalocyanine (**5**) (with perhaps 2,9-dineopentoxyphthalocyanine (**6**)) with a trace of the 2,9,16,23-tetraneopentoxyphthalocyanine (**8**) and some 2,9,16-trineopentoxyphthalocyanine (**7**), 2-neopentoxyphthalocyanine (**4**), and phthalocyanine (**3**). This fraction was purified by vacuum liquid chromatography (vlc) (23) using hexane (200 mL) as the eluting solvent, followed by hexane–toluene (1:1 × 700 mL) hexane–toluene (1:4 × 200 mL), toluene (500 mL), and finally 2-methoxyethanol–toluene (1:9 × 700 mL). The different fractions were examined by mass spectra (Table 3). Only partial separation was achieved.

The original mixture of phthalocyanines was subsequently extracted with toluene for 10 h and with THF for 19 h (extract 2) to give 27 mg of a mixture of phthalocyanines consisting mainly of monosubstituted phthalocyanine (**4**) and some unsubstituted, disubstituted, and a trace of trisubstituted phthalocyanines (Table 3). Further purification by vlc as above removed all trineopentoxyphthalocyanine but did not completely separate the dineopentoxyphthalocyanine from the mononeopentoxyphthalocyanine (Table 3). However, most of the unsubstituted phthalocyanine (**3**) was left on the column. The monosubstituted phthalocyanine (**4**) was recrystallized from toluene from a fraction (vlc fraction 3, Table 3) containing a trace amount of disubstituted phthalocyanine (**5**) but the crystallized product (**4**) still contained a trace of the disubstituted phthalocyanine (vlc fraction 3^e, Table 3).

Subsequent extraction of the original mixture with THF for 48 h (extract 3) removed 12.6 mg of a fraction consisting mainly of unsubstituted phthalocyanine (**3**) along with some **4** and a trace of **5** (Table 3). The phthalocyanines remaining in the thimble after the three extractions were the unsubstituted one and some monosubstituted (Table 3).

A synthesis of 2-neopentoxyphthalocyanine (4) (Experiment 2)

The crude 1,3-diiminoisoindoline derived from 2.0 g of phthalonitrile (15.6 mmol) in 15 mL of *N,N*-dimethylaminoethanol was heated to 120°C under an argon atmosphere for 2 h. Compound **10**, 135 mg (0.51 mmol), was then added and the mixture was kept at 120°C for an additional 3 h. The mixture was cooled to room temperature, diluted with water, filtered, and washed thoroughly with water followed by methanol until the filtrate was almost clear. The crude product was extracted with methanol in a Soxhlet apparatus until the extract was almost clear to remove brown and yellow impurities. The 1.56 g of the desired product was fractionally extracted with freshly distilled THF for 5 days. At intermittent times the solvent was evaporated, the phthalocyanines mixture was examined by mass spectra (Table 3), more solvent was added, and the extraction continued. The total amount of phthalocyanines removed by extraction after 5 days was 63.4 mg; 1.50 g was left in the thimble. The first extract contained a trace of **7**, some **5** (plus **6**), mainly **4** and **3** (Table 3). Subsequent extractions contained increasing amounts of the **5** and **4** without **7** (Table 3). During the last extraction a precipitate was formed which was filtered off to give 19.1 mg of mainly **3**, some **4**, and a trace of **5** (Table 3). The filtrate, 12.2 mg, contained **5** and **4** (Table 3).

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