to 4.9 kcal/mol, which is somewhat higher, but practically comparable with the inversion barrier for the symmetric C_2 mode.

The magnitude of the barrier determined for various inversion modes of **1** is not only in good agreement with those estimated for simple alicyclic compounds of comparable type, it also corresponds to rough estimations of the ring A inversion barrier of vitamins D. Based on NMR experiments,[10f] it was concluded that the upper limit of this barrier amounts to about 8.5 kcal/mol for the naturally occurring vitamins D. Thus, chair–chair interconversion is easily possible in these compounds, realizing the biologically active conformation at the receptor site.

Conclusions

Both ab initio basis sets provide a satisfactory description of the most important conformational aspects in the 1,2-dimethylenecyclohexane molecule, although the 3-21G results should be preferred with respect to the quantitative reproduction of geometry and energy data. A chairlike minimum structure is indicated, which may easily undergo ring inversion via an inversion/pseudorotation process as the most economical pathway. The dynamic behavior of the ring system of the title compound is generally comparable with that of the cyclohexane molecule. However, the introduction of the sp^2-hybridized carbons increases the ring mobility. The conformational data provide a good reference basis for a consideration of the ring-A properties of vitamin D derivatives but also for the discussion of the conformation of 2-methylenecyclohexanones[7i,23] and 1,2-cyclohexanediones.[7i,24] These structures are frequently realized in biologically active compounds.

Experimental Section

All calculations were performed within the ab initio SCF molecular orbital theory employing the STO-3G and 3-21G basis sets.[16] The geometries of the various conformations were completely optimized using the MONSTERGAUSS[17] and HONDO7[18] program systems. In order to characterize the critical points, the eigenvalues of the matrix of force constants were determined. In some special cases, the transition-state search procedure of the HONDO7 program package[19] was used. The character of the structures obtained in this way was confirmed by a separate force constant calculation.

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Synthesis and Characterization of Di-disubstituted Phthalocyanines

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An improved approach to the synthesis of di-disubstituted phthalocyanines from two different phthalyl precursors is described. The method combines substituted 1,3 diiminoisoindoles and 6/7-nitro-1,3,3-trichloroisoindolenine to synthesize phthalocyanine. The method can be applied to the synthesis of hydrogen and metallo phthalocyanine. The yields are variable, ranging from 17% to 72% depending on the substituents.

Phthalocyanine (Pc) has been the subject of a great deal of wide-ranging research for over 50 years.[1] This has led to over 7000 citations of Pc in *Chemical Abstracts*, most of which are patents.[2] The synthesis of a variety of substituted Pc's both metallo and nonmetallo have been reported.[3] The main purpose for these substitutions has been to enhance Pc's very limited solubility. These compounds have, with few exceptions, been synthesized by the tetramerization of a single type of substituted phthalyl compound. This results in the substitution of identical groups on all of the benzenoid rings, giving tetra, octa substitution or higher orders of four. The regioselectivity of this reaction is poor and gives mixtures of all possible orientation patterns for the substituents.

Exceptions to this synthetic approach are found in the work done by Lever and Leznoff[4] in the synthesis of mono-trisubstituted Pc's. This involved the polymer support of one type of substituted phthalyl unit and its reaction with a differently substituted phthalyl unit to form a Pc. However, this process is limited in the scope of potential Pc's synthesized.

Direct reaction of two different phthalyl compounds has been tried.[5] This led to a mixture of possible compounds of different substitutions and isomers. Lever and Leznoff[6] also synthesized their "clamshell" Pc by direct mixing of two different phthalyl units. This compound is interesting in that it contains two mono-trisubstituted Pc rings bound

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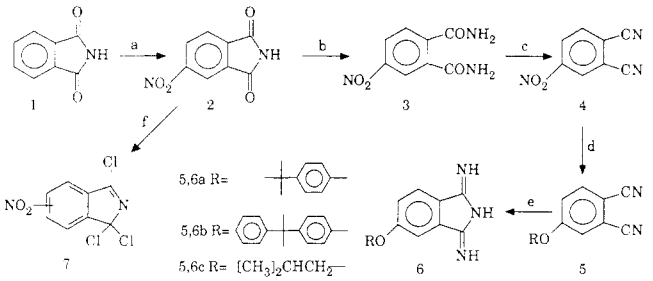
Scheme I[a]



[a] Reagents: (a) 100% HNO_3/H_2SO_4, 40 °C; (b) THF/NH_4OH, NH_3, 40 °C; (c) DMF, Cl_2SO; (d) DMSO, ROH, LiOH; (e) CH_3OH, CH_3ONa, NH_3; (f) DCB, PCl_5.

to each other through the monosubstituted unit. The isolation of this product required chromatographic separations and gave yields of less than 5%. We have reported attempting the use of a central metal atom as template to hold two phthalyl molecules in place while two different ones are added to make the ring.[7]

Direct synthesis of a di-disubstituted Pc has been reported by a patent.[8] The patent used the same materials reported here but ran the reaction in one step at high temperatures. Their yields were on the order of 5%. We have independently developed a similar stepwise procedure run under milder reaction conditions with higher yields, which we report here. This procedure involves the synthesis of Pc's from two different phthalyl derivatives to give a di-disubstituted Pc (**8**, **9**). Both hydrogen and metallo derivatives have been made. This route offers improved yields, with some general scope, of Pc's with substitution other than order of four.

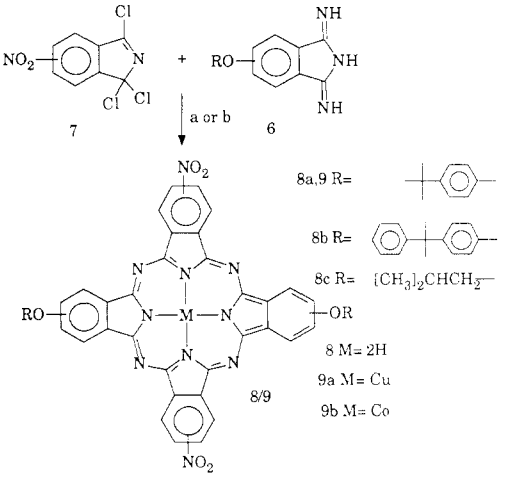
Results and Discussion

Scheme I shows the synthesis of the two phthalyl compounds used in this procedure. The synthesis of these compounds is reported for completeness and for some improvements over other reported preparations. The synthesis of 4-nitrophthalimide (**2**) that we developed for Scheme I is of note because of the milder conditions than that previously reported.[9] It also gave higher and more consistent yields (70%) of purified product. It was possible to scale this reaction up to as much as 250 g of phthalimide, although this does decrease the yields a few precent probably due to the inability to control the temperature as carefully.

4-Nitrophthalimide is used to produce both of the of the phthalyl compounds in this Pc synthesis. It is readily converted into the 4-nitrophthalamide (**3**) by the action of concentrated NH_4OH and NH_3 on a THF solution. The subsequent dehydration to 4-nitrophthalonitrile (**4**) was tried using a number of standard approaches. The use of the Vilsmeier reagent,[10] formed with thionyl chloride, was found to give the purest nitrile in the highest yield.

Nucleophilic substitution of 4-nitrophthalonitrile has been reported elsewhere.[6b,11] We have found the use of LiOH and longer reaction times to be a useful modification to the reported procedure. This is true not only for the nucleophiles used in this work, but also for others used in our laboratory.

Scheme II[a]



[a] Reagents: (a) THF, triethylamine, hydroquinone, CH_3ONa; (b) THF, MCl_2, triethylamine, hydroquinone, CH_3ONa.

The transformation of the substituted phthalonitriles (**5**) to diiminoisoindolines (**6**) followed the original Linstead preparation[12] with the addition of THF to enhance the solubility of these particular compounds. As has been pointed out before,[13] these compounds do not recrystallize well from the reported solvent systems. We were able to purify small quantities of these compounds through repeated treatments with decolorizing charcoal, but only by carefully controlling the temperature to below 45 °C and waiting long periods for the solid product. Even so, the product was usually a precipitated powder not a crystal. The compound was used as collected from the reaction solvent in all syntheses described here.

The conversion of the 4-nitrophthalimide to the 6/7-nitro-1,3,3-trichloroisoindolenine (**7**) was first reported in a patent in the early 1950s.[14] Since then, there have been only a small number of references to this compound and only one in a peer reviewed journal.[15] Based on the ^{13}C NMR data, the compound is a mixture of isomers with the nitro group at the 6- or 7-position. This compound and its derivatives will be discussed more fully in a subsequent paper.[16]

The synthesis of di-disubstituted metallo and hydrogen Pc is shown in Scheme II. While this reaction was attempted under various other conditions, those reported here were the best found. The yields by this process were significantly higher than those reported in the patent process.[8] The reaction is accompanied by several color changes. After the initial combination of the two compounds, the solution is a light yellow that changes to light yellow-green during the hold time. The addition of the strong base is accompanied by an immediate color change to dark blue which persists for the rest of the reaction. The color of the di-disubstituted Pc's tends more to the green than other tetrasubstituted Pc's. Further improvements in this reaction as to yield and purity may yet be achieved.

The synthesis of nickel di-disubstituted Pc was attempted, but only low yields of the resulting hydrogen di-disubstituted compound could be isolated. This may

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Table I. Visible Absorption Data for Di-disubstituted Phthalocyanine

compd	M	wavelength[a]/molar absorptivity (log ϵ)
8a	1.0×10^{-5}	693 (4.66),* 680 (4.73), 642 (4.53)
	5.0×10^{-6}	694 (4.77), 680 (4.84), 645 (4.54)
	1.0×10^{-7}	696 (4.94), 681 (5.00), 643 (4.53), 621 (4.43)*
8b	8.8×10^{-6}	693 (4.74),* 680 (4.81), 643 (4.59)
	4.4×10^{-6}	693 (4.85), 681 (4.91), 645 (4.59)
	8.8×10^{-7}	694 (4.99), 681 (5.04), 645 (4.54), 621 (4.45)*
8c	1.1×10^{-5}	696 (4.27),* 678 (4.38), 628 (4.49)
	5.5×10^{-6}	700 (4.43), 679 (4.53), 635 (4.53)
	1.1×10^{-7}	703 (4.77), 680 (4.86), 644 (4.62)
9a	1.0×10^{-5}	710 (4.54), 665 (4.54), 643 (4.45), 604 (4.18)*
	5.0×10^{-6}	710 (4.61), 665 (4.59), 643 (4.46), 603 (4.14)*
	1.0×10^{-6}	711 (4.59), 665 (4.71), 645 (457), 602 (4.25)
9b	9.2×10^{-6}	705 (4.45), 661 (4.34), 641 (4.32), 597 (4.00)*

[a] Values in nanometers. *Shoulder.

have been due to the lack of solubility of the Ni salt in the reaction mixture.

The initial purification of these compounds was done by boiling them in quantities of water until the filtrate was clear and repeating the process with ethanol. Purification of these compounds to analytical purity required size-exclusion chromatography on lipophilic Sephadex LH-20 in THF followed by chromatography on basic alumina.

Compound **9a** exhibits instability that is very uncharacteristic of Pc's. In dilute THF solution on standing for 48 h, the color changes form green to gray accompanied by disappearance of the visible Q band spectra. This also can occur to some extent on heating the compound in air at 60 °C. The exact nature of this decomposition is being investigated. The other Pc's reported are more stable by comparisons.

The IR spectra of these Pc's show the symmetric and asymmetric stretching of the nitro groups and the aryl ether stretching. The hydrogen Pc's also show the N–H stretch at 3296–3298 cm^{-1}. In general, they agree well with the other reported IR spectra of Pc's.[17]

The visible absorption spectra of these compounds, shown in Table I, differs in some ways from other substituted Pc's reported. The hydrogen di-disubstituted Pc's (**8**) show the expected splitting of the band around 680 nm. However the split is only 13–18 nm as compared to the 30 or more normally seen in hydrogen tetrasubstituted Pc.[18] For the metallo di-disubstituted Pc's (**9**), the splitting of the band is increased to 45 nm. This is counter to the normal spectra of metallo tetrasubstituted Pc's that have no splitting in this band. The difference can be attributed to the loss of symmetry from D_{4h} in the tetrasubstituted to D_{2h} in the di-disubstituted.[19] Upon dilution, the spectra of these compounds show shifts in band positions, changes in the molar absorptivities, and shifts in the relative intensities of the bands. This is likely due to a strong tendency to dimerize.[5] The effects of dilution on the spectra of these Pc's is shown in Table I.

The ^1H NMR data of compound **8** shows the typical strong shielding of the cavity hydrogens, absorbing around δ–10. The position of this peak has been shown to be concentration dependent[5] due to dimerization. FAB MS of compound **8a** gave the expected 901 $M^+ + 1$ peak. FAB spectra on other Pc's could not be obtained. This was probably due to difficulties with the matrix, 4-nitrobenzyl alcohol.

The possibility of 3 + 1 or 1 + 3 combinations of diimino and trichloro along with or instead of the 2 + 2 combinations seems to be very unlikely based on a number of pieces of evidence. The elemental analysis could only give the observed results if it were to contain one 1 + 3 for each 3 + 1. No peaks for either of these compounds were seen in the one FAB MS that was obtained. Also one of these would place three nitro groups on the Pc ring; tetranitro Pc is extremely insoluble. It is not likely that one solvating alkoxy group could impart enough solubility to make a pC with three nitros inseparable by the several solvents and two different chromatographic technics employed here.

There is no spectroscopic data to verify the trans assignment of the substitutions on the Pc ring. It is not likely that X-ray data would be of assistance due to the likelihood of positional isomerism usually present in the 4-substituted Pc's. However, the experimental conditions and the stepwise nature of the synthetic procedure lead to the conclusion that six of the nitrogens for the Pc ring come from the diimino starting material without cleavage, while the other two nitrogens come from the trichloro compound. Therefore, the trans assignment seems very reasonable.

Summary

We have presented a method for the synthesis of Pc's that are substituted with two different groups. This method is applicable to both metallo and hydrogen Pc's. We are investigating the scope of this reaction further.

Experimental Section

All melting points were determined on a Melt Temp and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 1600 FTIR or a Nicolet 5DX FTIR apparatus and are reported in cm^{-1}. Solids were run in KBr and liquids were run as thin films. Visible absorption spectra were obtained from a Bausch & Lomb Spectronic 2000 or a Perkin-Elmer Lamba 3 with tetrahydrofuran or chloroform as the solvent and are reported in nanometers. Nuclear magnetic resonance spectra were obtained in either deuterated chloroform or deuterated methylene chloride as indicated on a JEOL FX 90-Q, a Bruker 200, or an IBM NR200 instrument using tetramethylsilane (tMS) as the internal standard. Mass spectral data were collected on a Hewlett-Packard 5985-A GC/MS system by direct insertion and are reported in amu. FAB MS data were obtained on a Kratos MS 50 with 4-nitrobenzyl alcohol as the matrix. Chemical analyses were performed by Atlantic Microlabs, Atlanta, GA.

4-Nitrophthalimide (2). To 250 mL of a mixture of concentrated sulfuric acid and 100% nitric acid[20] (4:1 v/v) at 15 °C was added 40.0 g (0.272 mol) of phthalimide (Aldrich Chemical Co.) in portions over a 15-min interval with stirring. The temperature was raised slowly to 35 °C and held for 45 min. The solution turned yellow in color. The product mix was cooled to 0 °C, slowly stirred into 1 kg of ice at a rate such that the temperature was kept below 15 °C, collected by vacuum filtration, and washed with cold water.

The product was recrystallized from ethanol to give buff-colored, platelike crystals: yield 36.5 g (70%); mp 194.5–195 °C; IR 3320 (s), 3090 (w), 3040 (w), 1540 (s), 1343 (s), 1785 (m), 1700 (s), 1615 (m), 1305 (s), 1108 (m), 1075 (s), 718 (s); MS M^+ 192 (97%), $M^+ + 1$ (11.5% of M^+), $M^+ + 2$ (2.0% of M^+), 103 (100%).

4-Nitrophthalamide (3). To 500 mL of THF was added 50 g (0.26 mol) of 4-nitrophthalimide, and the mixture was heated to 40 °C with stirring; 360 mL of concentrated ammonium hydroxide was added to the solution, and a precipitate formed. NH_3 was bubbled through the reaction mixture for 2 h. The reaction mixture was cooled to 0 °C, and the product was isolated by vacuum filtration to give 40 g (73%) of dry product: mp 197 °C; IR 3410 (s, br), 3300 (s), 3180 (s), 3060 (w), 1655 (s), 1605 (s), 1515

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(s), 1380 (m), 1345 (s), 795 (s); MS M^+ 209 (5%), $M^+ + 1$ (10% of M^+), 193 (100%).

4-Nitrophthalonitrile (4). To 70 mL of dry DMF at 0 °C in a 500-mL round-bottom flask equipped with a magnetic stirrer, a thermometer, and a $CaCl_2$ drying tube was slowly added 7.3 mL of thionyl chloride. The temperature was kept below 5 °C during the addition, and the reaction mixture was stirred for 10 min; 10.0 g (0.048 mol) of 4-nitrophthalamide was added in portions over a 10-min period with the temperature kept below 5 °C. The reaction mixture was stirred for an additional 45 min at this temperature and 2 h while allowed to warm to room temperature. After this, the reaction mixture was stirred into 200 mL of ice. The product was collected by vacuum filtration was washed with three 500-mL portions of water and 500 mL of 5% sodium bicarbonate solution.

The product was air dried at 50 °C and gave 7.4 g (90%): mp 141 °C; IR 3090 (m), 3030 (w), 2230 (m), 1600 (m), 1530 (s), 1345 (s), 1580 (m), 795 (m); MS M^+ 173 (100%), $M^+ + 1$ (9%), $M^+ + 2$ (1%), 127 (93%).

4-(*p*-*tert*-Butylphenoxy)phthalonitrile (5a) (Representative Procedure). To 60 mL of DMSO at 25 °C were added 1.73 g (10 mmol) of 4-nitrophthalonitrile and 1.50 g (10 mmol) of *p*-*tert*-butylphenol. The reaction mixture was stirred, and 0.60 g (25 mmol) of LiOH was added over a 2-h period. The reaction was then stirred for 3 days. Aliquots were taken periodically to check for completeness of reactions by monitoring the aryl nitro bands in the IR of samples. The reaction mixture was then poured slowly into 5 times the volume of 10% NaCl solution with stirring. After the mixture was stirred for 1 h, the product was collected by vacuum filtration.

The crude product was decolorized and recrystallized from ethanol and gave 1.88 g (6.8 mmol) (68%): mp 118–9 °C; IR 3080 (w), 3055 (w), 2960 (s), 2870 (w), 2230 (m), 1585 (s), 1485 (s), 1245 (s), 1022 (m); MS M^+ 276 (17%), $M^+ + 1$ (21% of M^+), $M^+ + 2$ (2.3% of M^+), 261 (100%).

4-(*p*-Cumylphenoxy)phthalonitrile (5b): mp 88 °C (lit.[21] mp 90 °C); IR 3080 (w) 3060 (w), 3030 (w), 2973 (s), 2931 (w), 2230 (m), 1580 (s), 1485 (s), 1250 (s), 1022 (m); MS M^+ 338 (31%), $M^+ + 1$ (25% of M^+), $M^+ + 2$ (24.6% of M^+), 323 (100%).

4-Isobutoxyphthalonitrile (5c): mp 34–36 °C (lit.[22] mp 49–49.5 °C); IR 3080 (w), 2970 (s), 2945 (w), 2890 (w), 2235 (m), 1600 (s), 1497 (s), 1260 (s), 1006 (m); MS M^+ 200 (100%), $M^+ + 1$ (14%), $M^+ + 2$ (1.1%), 143 (77%).

6-(*p*-*tert*-Butylphenoxy)-1,3-dihydro-1,3-diiminoisoindole (6a) (Representative Procedure). To 80 mL of a dry methanol and THF (50:50 v:v) in a round-bottom flask equipped with a magnetic stirrer, a reflux condenser, and an ammonia gas inlet were added 0.01 g of sodium methoxide and 2.00 g (7.2 mmol) of 4-substituted phthalonitrile. Ammonia was bubled through, and the solution was stirred at room temperature for 1 h. The solution was then heated to reflux for 2 h with continued addition of ammonia. After refluxing the mixture was added to an equal volume of 10% NaCl solution and extracted three times with diethyl ether. The ether extracts were combined, washed three times with saturated NaCl to remove any remaining THF, and dried.

The product slowly crystallized out of the ether on standing and was dried under vacuum at 40 °C. The typical product was light green in color and could be decolorized with great difficulty from aqueous ethanol. The yield was 1.31 g (62%): mp 206 °C; IR 3290 (br, w), 3056 (w) 3031 (w), 2963 (s), 2870 (w), 1603 (s), 1537 (s), 1476 (s), 1234 (s); MS M^+ 293 (27%), $M^+ + 1$ (22% of M^+), $M^+ + 2$ (2.6% of M^+), 278 (100%); ^1H NMR 7.69–6.95 (m, 7 H), 5.80 (br, 3 H), 1.35 (s, 9 H).

6-(*p*-Cumylphenoxy)-1,3-dihydro-1,3-diiminoisoindole (6b): mp 192 °C; IR 3240 (br, w), 3086 (w), 3054 (w), 3027 (w), 2969 (s), 2870 (w), 1603 (s), 1537 (s), 1476 (s), 1233 (s), 1015 (w); MS M^+ 355 (56%), $M^+ + 1$ (15% of M^+), 340 (100%); ^1H NMR 7.69–6.95 (m, 11 H), 5.80 (br, 3 H), 1.71 (s, 6 H).

6-Isobutoxy-1,3-dihydro-1,3-diiminoisoindole (6c): mp 162 °C; IR 3275 (br, w), 3052 (w), 2958 (s), 2869 (w), 1620 (s), 1537 (s), 1487 (s), 1230 (s), 1023 (w); MS M^+ 217 (15%), $M^+ + 1$ (14% of M^+), 161 (100%); ^1H NMR 7.80–6.97 (m, 3 H), 5.80 (br, 3 H), 3.86 (d, 2 H), 2.14 (m, 1 H), 1.08 (d, 6 H).

6/7-Nitro-1,3,3-trichloroisoindolenine (7). In a 100-mL round-bottom flask equipped with a magnetic stirrer, reflux condenser, and $CaCl_2$ drying tube were combined 4.8 g (0.025 mol) of 4-nitrophthalimide, 11.0 g (0.053 mol) of PCl_5, and 20 mL of dry 1,2-dichlorobenzene. The reaction mixture was heated to 105 °C. After approximately 30 min the mixture was sufficiently liquid to stir. The reaction was heated and stirred for 1 week.

The reaction mixture was then cooled to room temperature and stirred vigorously while aspirator vacuum was slowly applied to strip volatiles from the reaction mixture. When full aspirator vacuum had been applied and the frothing subsided, all of the $POCl_3$ reaction byproduct and most of the dichlorobenzene solvent was distilled off by heating to 110 °C.

The product was a light yellow oil isolated by fractional vacuum distillation (bp 125 °C to 0.05 Torr) in a 35% yield. This oil tended to form a red solid on long standing: IR 3103 (w), 3050 (w), 1760 (m), 1742 (m), 1616 (w), 1550 (s), 1533 (s), 1344 (s), 1266 (m), 855 (s), 824 (s); ^{13}C NMR 163.34, 163.12, 156.35, 152,83, 150.61, 149.58, 136.47, 133.65, 128.07, 126.99, 123.68, 123.09, 117.99, 117.67, 98.49; MS M^+ 264 (2%), $M^+ + 2$ 266 (100% of M^+), 229 (100%). Anal. Calcd. for $C_8H_3N_2O_2Cl_3$: C, 36.18; H, 1.13; N, 10.55. Found: C, 36.41; H, 1.21; N, 10.64.

4,4‴-Bis(4-*tert*-butylphenoxy)-4′,4‴-dinitrophthalocyanine (8a) (Representative Procedure). In a dried 100-mL round-bottom falsk equipped with a magnetic stirrer and sealed with a septum were placed 0.100 g (0.34 mmol) of 6-(4-*tert*-butylphenoxy)diiminoisoindoline and 0.069 g (0.068 mmol, 1.5 equiv) of triethylamine. Dry nitrogen was swept through the flask by the two-needle method; 30 mL of freshly dried THF was added with a syringe, and the mixture was stirred to dissolve the diiminoisoindoline. The mixture was then cooled to approximately 0 °C in a salt and ice bath. A solution of 0.090 g (0.34 mmol) of 6/7-nitro-1,3,3-trichloroisoindolenine in 10 mL of dry THF was gradually added by syringe over a 15-min period. The reaction was then stirred for 1 h at approximately 0 °C and allowed to slowly warm to room temperature with stirring over a 6-h period. During this time, the reaction turned from its initially formed yellow to a yellow-green.

The reaction was then filtered to remove the triethylammine hydrochloride and returned to the reaction flask; 0.037 g (.34 mmol) of hydroquinone and 0.054 g (1 mmol) of sodium methoxide were added to the reaction vessel, which was then equipped with a reflux condenser. It was then refluxed under nitrogen for 6 h. The reaction was cooled to room temperature and filtered, and the solvent was stripped from the filtrate leaving a dark blue-black residue.

The residue was washed by boiling in water and filtering until the filtrate was clear; this procedure was repeated with ethanol. The yield of 4,4‴-bis(4-*tert*-butylphenoxy)-4′,4‴-dinitrohydrogenphthalocyanine was 48%. The product could be further purified by chromatography on Sephadex LH 20 with THF as the sovlent. For purposes of elemental analysis it was necessary to further purify it on basic alumina using cyclohexane/THF (90/10 to 50/50) as the solvent: IR 3297 (w), 3094 (w), 3066 (w), 3040 (w), 2969 (s), 2870 (w), 1613 (w), 1602 (s), 1527 (s), 1487 (s), 1340 (s), 1234 (s); FAB MS (P + 1) 901; ^1H NMR 7.83–6.17 (m v br, 28 H), 1.54 (s br, 32 H), −10.6 (s br, 2 H); UV (5.0×10^{-6} M in THF) (log ϵ) 694 (4.77), 680 (4.84), 645 (4.54). Anal. Calcd. for $C_{52}H_{40}N_{10}O_6$: C, 69.32; H, 4.47; N, 15.55. Found: C, 69.01; H, 4.77; N, 15.23.

4,4‴-Bis(4-cumylphenoxy)-4′,4‴-dinitrophthalocyanine (8b): yield 48%; IR 3296 (w), 3087 (w), 3057 (w), 3033 (w), 2969 (s), 2870 (w), 1613 (w), 1601 (s), 1527 (s), 1476 (s), 1339 (s), 1234 (s); ^1H NMR 7.17–6.17 (m v br, 48 H), 1.57 (s br, 24 H), 2.14 (m, 1 H), 1.08 (d, 6 H), −10.3 (s br, 2 H); UV (4.4×10^{-6} M in THF) (log ϵ) 693 (4.85), 68 (4.91), 645 (4.59). Anal. Calcd. for $C_{62}H_{44}N_{10}O_6$: C, 72.64; H, 4.33; N, 13.66. Found: C, 72.92; H, 4.69; N, 13.29.

4,4‴-Diisobutoxy-4′,4‴-dinitrophthalocyanine (8c): yield 17%; IR 3298 (w), 3095 (w), 2961 (s), 2934 (m), 2870 (w), 1616 (w), 1610 (s), 1526 (s), 1469 (s), 1339 (s), 1239 (s), 1030 (m); ^1H NMR 8.05–6.58 (m v br, 12 H), 3.68 (d, 8 H), 1.94 (m, 4 H), 1.04 (d, 24 H), −10.8 (s v br, 2 H); UV (5.5×10^{-6} M in THF) (log ϵ) 700 (4.43), 679 (4.53), 635 (4.53). Anal. Calcd. for $C_{40}H_{32}N_{10}O_6$: C, 63.08; H, 5.83; N, 18.41. Found: C, 62.80; H, 5.98; N 18.09.

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[4,4‴-Bis(4-cumylphenoxy)-4′,4‴-dinitrophthalocyaninato(2-)]copper(II) (9a) (Representative Procedure). The reaction was the same as the representative procedure up to the removal of the triethylamine hydrochloride. At this point 0.038 g (0.28 mmol) of anhydrous cuprous chloride was added to the reaction mixture, and it was stirred under nitrogen for 13 h at room temperature. After this time 0.046 g of sodium methoxide and 0.062 g of hydroquinone were added to the reaction mixture, and it was refluxed and stirred for an additional 6 h. The solvent was then stirred and the solid was purified as before: yield 72%; IR 3086 (w), 3058 (w), 3030 (w), 2966 (s), 2930 (w), 1613 (w), 1600 (s), 1533 (s), 1476 (s), 1339 (s), 1234 (s); ^{1}H NMR 7.26–6.95 (m br, 24 H), 1.53 (s br, 32 H); UV (5.0×10^{-6} M in THF) (log ϵ) 710 (4.61), 665 (4.59), 643 (4.46), 603 (4.14). Anal. Calcd. for $C_{52}H_{38}N_{10}O_6Cu$: C, 68.53; H, 3.89; N, 12.89. Found: C, 68.30; H, 4.15; N, 12.61.

[4,4‴-Bis(4-cumylphenoxy)-4′,4‴-dinitrophthalocyaninato(2-)]cobalt(II) (9b): yeild 58%; IR 3086 (w), 3058 (w), 3030 (w), 2965 (s), 2971 (w), 1613 (w), 1601 (s), 1527 (s), 1474 (s), 1333 (s), 1234 (s); ^{1}H NMR 7.30–6.80 (m br, 24 H), 1.56 (s br, 32 H); UV (9.2×10^{-6} M in THF) (log ϵ) 705 (4.45), 661 (4.34), 641 (4.32), 597 (4.00). Anal. Calcd. for $C_{52}H_{38}N_{10}O_6Co$: C, 68.82; H, 4.10; N, 12.95. Found: C, 68.59; H, 4.27; N, 12.63.

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Registry No. **2**, 89-40-7; **3**, 13138-53-9; **4**, 31643-49-9; **5a**, 125023-51-0; **5b**, 83482-57-9; **5c**, 96917-81-6; **6a**, 125023-52-1; **6b**, 125023-53-2; **6c**, 96917-83-8; **7** (6-NO_2), 41645-42-5; **7** (7-NO_2), 41645-43-6; **8a**, 125023-55-4; **8b**, 125023-56-5; **8c**, 125023-57-6; **9a**, 125023-54-3; **9b**, 125048-81-9; *p-tert*-butylphenol, 98-54-4; ammonia, 7664-41-7; phthalimide, 85-41-6.

Superoxide Oxidation: A Novel Route to Aromatic 1,2-Dicarboxylic Acids

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Potassium superoxide in aprotic media, in the presence of 18-crown-6 ether, effects a novel and mild oxidative cleavage of quinones, cyclic alcohols, and ketones fused to various aromatic hydrocarbons. Aromatic 1,2-dicarboxylic acids are obtained as major products, with highest yields in dimethylformamide, under oxygen or air. For example, the yield of pyrene-1,2-dicarboxylic acid is 82% from 9,10-dihydrobenzo[*a*]pyren-7(8*H*)-one and 88% from benzo[*a*]pyrene-7,8-dione. Minor side products include aromatic tetrones and 3-(2-carboxyaryl)propionic or 3-(2-carboxyaryl)propenoic acid, which provide mechanistic insights.

The chemical reactivity including mechanistic details for the reaction of potassium superoxide (KO_2) with organic substrates has been reviewed.[1,2] Two general reactivity patterns of KO_2 predominate in aprotic media depending on the substrate: oxidations and nucleophilic displacements. For the oxidations, H_2O_2 and O_2 generated in situ, along with O_2 bubbled through the reaction mixture, are the true oxidants.[1] Typically, the reactions are carried out in the presence of a crown ether to increase the solubility of KO_2 in aprotic solvents such as DMF, THF, toluene, or benzene.

One type of product that arises from the oxidative cleavage of susceptible substrates with KO_2 is an organic acid or diacid. San Fillipo, Jr., et al.[3] successfully used KO_2 to oxidatively cleave a series of α-keto, α-hydroxy, and α-halo carboxylic acids, esters, and ketones to the corresponding carboxylic acids. Moreover, it has been reported that diphenic acid is obtained from the KO_2 oxidation of 9,10-dihydroxyphenanthrene or the corresponding quinone.[4]

Among such KO_2 reactions, however, are lacking any reports of aromatic 1,2-dicarboxylic acid products. In fact, the literature indicates that such products are not obtained even when potential precursors are reacted with KO_2. For example, reaction of α-tetralone with KO_2 in toluene yields α-naphthol (38%) and 2-hydroxy-1,4-naphthoquinone (10%). Similar reaction of β-tetralone gives the latter product (27%), β-naphthol (5%), and 3-(2-carboxyphenyl)propionic acid (14%).[5] Using a higher concentration of KO_2 in THF, others have obtained a 75% yield of 2-hydroxy-1,4-naphthoquinone from both α- and β-tetralone.[6] The latter product is also isolated in 60% yield from the KO_2 reaction of either 1,2- or 1,3-dihydroxynaphthalene.[7] In another case, the reaction of KO_2 with 1,2-naphthoquinone is reported[2,8] to yield *cis*-2-carboxycinnamic acid and 2,3-benzo-4-(carboxymethyl)butyrolactone, although we question the stereochemistry assigned to the former product (see below).

In contrast, here we report that high yields of aromatic 1,2-dicarboxylic acids can be obtained by the reaction of KO_2 with any of the above precursors, and various related compounds. This is essentially achieved by balancing the molar ratio of KO_2:crown ether:substrate in an appropriate solvent, under oxygen or air.

Results and Discussion

Table I summarizes the reactions that we have conducted with KO_2. As can be seen, a variety of aromatic

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