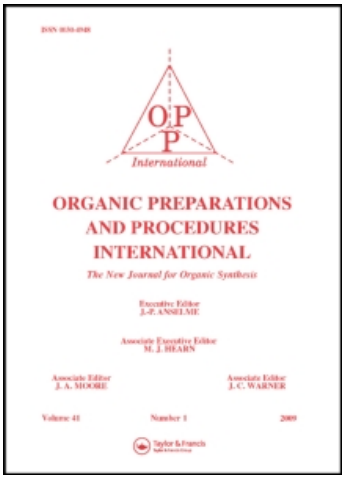

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IMPROVED SYNTHESIS OF *cis*-9,10-DIHYDRO-9,10,-PHENANTHRENEDICARBOXIMIDES AND 9,10-PHENANTHRENEDICARBOXIMIDES

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J = 7.5 Hz, 4 H), 3.56 (s, 4 H), 4.14 (s, 4 H); ^{13}C NMR ($CDCl_3$): δ 14.0, 22.6, 24.8, 29.1-29.5 (5 signals), 31.8, 44.6, 62.2, 62.3, 174.3.

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IMPROVED SYNTHESIS OF *cis*-9,10-DIHYDRO-9,10-PHENANTHRENEDICARBOXIMIDES AND 9,10-PHENANTHRENEDICARBOXIMIDES

Submitted by (02/22/99)

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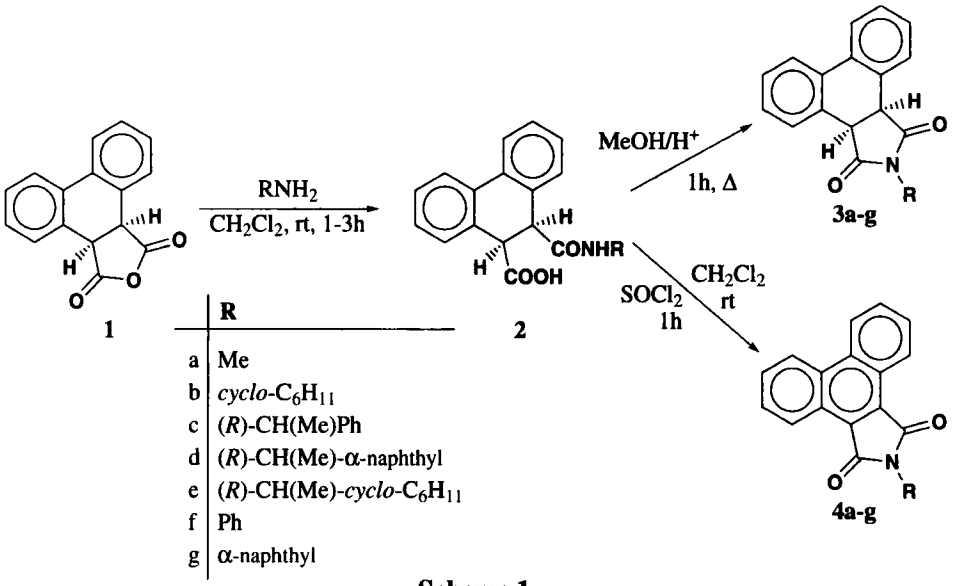
Aromatic imides play an important role in synthesis (amine group protection,[1] intramolecular cyclization reactions)[2] as well as in pharmaceutical, pigment and materials science applications.[3] 9,10-Phenanthrenedicarboximides (**4**) and their 9,10-dihydro derivatives **3** are less explored group of aromatic imides due to the difficulty in their preparation. Reported condensations of *cis*-9,10-dihydro-9,10-phenanthrenedicarboxylic anhydride (**1**) or 9,10-phenanthrenedicarboxylic anhydride with methylamine led to the corresponding *N*-methylimides **3a**[4] and **4a**[5] in low yields. *N*-Methylimide **4a**

was also obtained, along with other products, by anellating photosubstitution of the bromine in *N*-methyl dibromomaleimide with biphenyl.[6,7]

cis-9,10-Dihydro-9,10-phenanthrenedicarboxylic anhydride (**1**) is available from phenanthrene by the method of Jeanes and Adams,[8] as modified by Rio and Berthelot.[9] 9,10-Phenanthrenedicarboxylic anhydride can be obtained from **1** by oxidation.[8] It is also a product of other processes, such as the Diels-Alder reaction of 1-phenylcyclohexene with maleic anhydride[10] or bicyclohexenyl with maleic anhydride[11] followed by dehydrogenation; from 2-phenylbenzoic acid;[12] or by irradiation of a solution of diphenylmaleic anhydride in the presence of oxygen.[13] However the use of 9,10-phenanthrenedicarboxylic anhydride for the preparation of imides **4** is limited by its low solubility in common organic solvents.

We have found that imides **3** and **4** can be obtained in a simple and high-yield way from *cis*-anhydride **1**. Treatment of **1** with a primary amine at room temperature gives the monoamide **2** in nearly quantitative yield. Subsequent ring closure to the *cis*-imides **3** occurs under mild conditions (acidic methanol) with overall yield 58-92%. On the other hand, treatment of **2** with thionyl chloride at room temperature results in ring closure to give yellow colored imides **4** with high overall yield. In this reaction, thionyl chloride apparently acts as an oxidant of the activated C-H bonds,[14,15] prior to the formation of the imide ring (imides **3** are not oxidized to **4** by the action of thionyl chloride under identical conditions).



Scheme 1

EXPERIMENTAL SECTION

IR spectra were obtained on a Perkin Elmer 580 spectrophotometer, as KBr pallets. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian EM-360 spectrometer with TMS as an internal standard. MS spectra were determined with an AMD 604/402 spectrometer. Melting points are uncorrected. Optical rotations were measured with a Perkin Elmer 243B polarimeter.

TABLE 1. Data for Imides **3a-3h** and **4a-4h**

Cmpd	Yield (%)	Mp. (°C)	IR (KBr) n (cm^{-1})	^{1}H NMR δ, *J* (Hz)	^{13}C NMR δ, *J* (Hz)	$[\alpha]_D$ (c=1,$CHCl_3$)	Elemental Analysis (%) Theor.	Found
3a	58	203-205[a]	1775, 1702	3.00 (s, 3H), 4.35 (s, 2H), 7.32-7.42 (m, 4H), 7.72-7.75 (m, 2H), 7.90-7.94 (m, 2H)	25.5, 43.2, 123.4, 126.8, 128.3, 128.6, 129.9,131.1, 177.1		C 77.55	77.63
							H 4.98	4.49
							N 5.32	5.07
3b	72	178-180	1770, 1695	1.13-2.13 (m, 10H), 3.70-4.0 (m, 1H), 4.26 (s, 2H), 7.26-7.41 (m, 4H), 7.68-7.72 (m, 2H), 7.89-7.92 (m, 2H)			C 79.73	79.65
							H 6.39	6.54
							N 4.23	4.15
3c	92	149-151	1778, 1700	1.72 (d, 3H, *J* = 7.2), 4.24 (d, 1H, *J* = 9.6), 4.29 (d, 1H, *J* = 9.6), 5.39 (q, 1H, *J* = 7.2), 7.2-7.4 (m, 9H), 7.65-7.70 (m, 2H), 7.9-7.95 (m, 2H)	16.5, 43.4, 50.7, 123.5, 126.9, 127.0-139.3 (C_{arom}), 176.6, 176.7	+ 21.4	C 81.56	81.24
							H 5.42	5.22
							N 3.96	3.87
3d	68	160-163	1774, 1702	1.88 (d, 3H, *J* = 7.0), 4.18 (d, 1H, *J* = 9.6), 4.24 (d, 1H, *J* = 9.6), 7.2-7.9 (m, 15H)	17.1, 43.4, 46.9, 122.6-133.6 (C_{arom}), 176.5, 176.7	+ 6.7	C 83.35	83.09
							H 5.25	5.42
							N 3.96	3.50
3e	78	126-130	1778, 1707	0.9-1.9 (m, $11H_{cyclohexyl}$), 1.29 (d, 3H, *J* = 6.8), 3.81(m, 1H), 4.28 (s, 2H), 7.26-7.42 (m, 4H), 7.66-7.71 (m, 2H), 7.89-7.92 (m, 2H)		+ 5.3	C 80.19	79.93
							H 7.01	6.80
							N 3.90	3.65
3g	74	196-198	1776, 1705	4.51 (s, 2H), 7.20-7.45 (m, $9H_{arom}$), 7.74-7.77 (m, 2H), 7.89-7.93 (m, 2H)			C 81.21	81.01
							H 4.65	4.61
							N 4.30	4.22
3h	70	228-230	1780, 1710	4.10 (s, 2H), 7.08 (d, 1H, *J* = 7.3), 7.4-7.55 (m, 5H), 7.6-7.7 (m, 3H), 7.78 (d, 1H, *J* = 7.6), 7.95-8.1 (m, 4H)[c]			C 83.18	82.84
							H 4.56	4.86
							N 3.73	3.68

TABLE 1. Continued...

Cmpd	Yield (%)	Mp. (°C)	IR (KBr) n (cm^{-1})	^1H NMR δ, *J* (Hz)	^{13}C NMR δ, *J* (Hz)	$[\alpha]_D$ (c=1,$CHCl_3$)	Elemental Analysis (%) Theor.	Found
4a	88	223-225[b]	1755, 1703	3.23 (s, 3H), 7.7-7.8 (m, 4H), 8.65-8.68 (m, 2H), 9.06-9.09 (m, 2H)	23.7, 123.0, 125.3, 126.1, 127.4, 128.3, 129.2, 133.1, 169.8			
4b	77	272-274	1756, 1698	1.25-2.34 (m, 10H), 4.12-4.23 (m, 1H), 7.72-7.82 (m, 4H), 8.66-8.71 (m, 2H), 9.11-9.14 (m, 2H)			C 80.22 H 5.81 N 4.25	79.92 5.84 4.18
4c	95	176-181	1778, 1704	1.70 (d, 3H, *J* = 7.0), 5.48 (q, 1H, *J* = 7.0), 7.25-7.65 (m, 5H), 7.75-7.90 (m, 4H), 8.70-8.74 (m, 2H), 8.99-9.03 (m, 1H), 9.46-9.48 (m, 1H)	25.05, 58.5, 123-144.8 (C_{arom}), 165.1	+3.8	C 82.03 H 4.88 N 3.99	81.84 4.98 3.78
4d	70	202-205	1762, 1708	1.83 (d, 3H, *J* = 6.6), 6.24 (q, 1H, *J* = 6.6), 7.5-7.85 (m, $7H_{arom}$), 7.88 (m, 2H), 8.05 (d, 1H, *J* = 7.1), 8.41 (d, 1H, *J* = 8.2), 8.72 (m, 2H), 9.01(m., 1H), 9.54 (m, 1H)	24.5, 55.3, 123.1-148.2 (C_{arom}), 165.23	- 48.8	C 83.77 H 4.77 N 3.49	83.43 4.50 5.51
4e	69	162-167	1757, 1704	0.95-2.1 (m, $11H_{cyclohexyl}$), 1.54 (d, 3H, *J* = 7.0), 4.04-4.22(m, 1H), 7.74-7.84(m, 4H), 8.73-8.78 (m, 2H), 9.14-9.18 (m, 2H)		+ 2.5	C 80.64 H 6.49 N 3.92	80.44 6.18 3.90
4g	83	272-274	1766, 1710	[d]			C 86.35 H 2.25 N 3.47	81.40 3.98 4.13
4h	75	282-285	1760, 1700	[d]			C 83.63 H 4.05 N 3.75	83.37 4.10 3.85

a) *lit.*[4] mp. not reported. b) *lit.*[6,7] mp. 226-228°, 224-226°. c) in CD_2Cl_2/TFA solvent. d) insufficient solubility

***N*-Methyl 9,10-dihydro-9,10-*cis*-phenanthrenedicarboximide (3a). Representative Procedure**.- A solution of anhydride **1**[8,9] (0.125g, 0.5 mmol) in CH_2Cl_2 (5mL) was treated at ambient temperature with methylamine (0.1mL, 6M solution in methanol). After stirring 2h the solvents were removed *in vacuo* and to the residual amidoacid **2a** was added methanol (3mL) and 3-4 drops conc. H_2SO_4. After refluxing for 1h the solution was allowed to cool to ambient temperature and the product (**3a**) was collected and recrystallized from methanol to give 0.076g (58%), mp. 203-205°, lit.[4] mp. not reported; MS: *m/z* 263(M^+), 178.

As a side-product, the intermediate methyl ester of amidoacid **2a** could be separated, mp. 202-204°, ^1H NMR ($CDCl_3$/TMS): δ 2.74(d, 3H, J = 5.0), 3.72 (s, 3H), 4.14 (dd, 2H), 5.80 (broad s, 1H), 7.25-7.95 (m, 8H).

This procedure was repeated on a larger scale with 1.0g (4 mmol) anhydride **1** and (*R*)-(+)-α-methylbenzylamine (0.5g, 4.1 mmol). Yield of the product (**3c**) was 1.2g (91%), mp.148-151°.

***N*-Methyl 9,10-phenanthrenedicarboximide (4a): Representative Procedure**.- Crude amidoacid **2a** (0.5mmol) was prepared as described for **3a** and dissolved in CH_2Cl_2 (3mL). To this solution was added thionyl chloride (0.11 mL, 1.5 mmol) and the solution was stirred at ambient temperature for 1h. During this time the solution turned yellow. The mixture was diluted with CH_2Cl_2, extracted with 10% aq. $NaHCO_3$, the extract dried with $MgSO_4$ and evaporated to give yellow product (**4a**), yield 0.114g (88%). The product was recrystallized from methanol, mp. 223-225°, *lit.*[6,7] mp. 226-228°, 224-226°; MS: m/z 261(M^+), 217, 176.

On a larger scale the intermediate amidoacid **2c** (4 mmol) was treated with thionyl chloride (0.66 mL, 9 mmol) to give the product (**4c**), mp. 174-179°, with the yield 92%.

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PREPARATION OF 3-TETRADECYLINDOLE

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To date, no comprehensive synthetic technique has been developed for the synthesis of 3-substituted long chain alkyl indoles. However, two reports for the synthesis of 3-octylindole do exist in the literature.[1,2] Since we required a number of examples of these alkyl indoles for testing their effect on sediment formation in fuels, we made a study of feasible synthetic techniques.[3]

Numerous attempts to synthesize short chained 3-alkylindoles have been reported.[4] Most involved the use of an organometallic species in varying yields, one of which includes the use of a nickel-phosphine complex to aid the cross-coupling of indole with an alkyl halide.[5] Alkylation of indole has also been reported to occur when $ZnCl_2$ and $Zn(OAc)_2$ are employed, albeit in low yields.[6] Other approaches include the use of iron complexes[7] and copper complexes.[8] Reports of reactions