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Preparation of *N*-arylmaleimides with PPh_3-$CBrCl_3$ as reagent

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Abstract *: N-Arylmaleimides have been prepared from maleic acid monoaryl amides by the action of PPh_3-$CBrCl_3$ in the presence of trimethylamine using acetonitrile as solvent.*
Keywords: *Intramolecular imidation, modified Appel reagent, UV-VIS spectroscopy*

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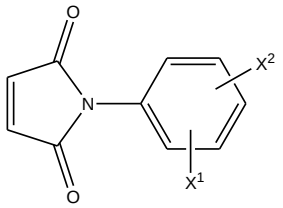
I. Introduction

N-substituted maleimides **1** are versatile dienophiles in [4+2]-cycloaddition reactions [1,2] and reactive Michael acceptors [3,4]. Also, maleimides have been used as monomers in polymerization reactions to polyimides [5-8], which function as high temperature resins. The polymers are obtained through iterative cycloaddition reactions [9,10], Michael addition [11], or by free-radical mechanisms [12], where especially *ortho*-substituted maleimides can act as radical initiators under photoirradiation [13]. In addition, maleimides have been used as starting materials in tumour-drug research [4] and as linker units in further biochemical studies [14,15]. In their own right, *N*-arylmaleimides have been found to be fungicidal vs. *Candida albicans* and other *Candida* species [16].

N-Arylmaleimides **1** can be synthesized in a number of ways, where for many of the methods maleic anhydride (2) is the starting material. One of the most commonly used methods is a two step approach where anilines are reacted with maleic anhydride (**2**) first to give maleanilic acids **4** (see Scheme 1). In the next step maleanilic acid is reacted with NaOAc/Ac_2O, where acetic anhydride (Ac_2O) is also used as the solvent [17-19]. Other methods involve the ring closure of maleanilic acids **4** to *N*-arylmaleimides **1** utilizing the reagents acetyl chloride / triethylamine [20], trimethyl orthoacetate / triethylamine [21], or methanesulfonic acid in *n*-butanol [22]. Alternatively, there are limited ways to produce *N*-arylmaleimides **1** directly from maleic anhydride (**2**) via the reaction with anilines **3** such as when utilizing HMDS/$ZnBr_2$ [23] or $(NH_4)_2S_2O_8$–DMSO [24] from the reaction of maleic acid with anilines **3** in the presence of phosphorus pentoxide [25]. In our previous interest to utilize *N*-arylmaleimides as dienophiles [2,26], we prepared the compounds via the more common method mentioned above, using NaOAc/Ac_2O, but noted that during the work-up the necessary hydrolysis and subsequent neutralization of the excess amount of Ac_2O with Na_2CO_3 produced a lot of CO_2. As we were submitting the final product mixtures to a rapid column chromatography to obtain highly pure *N*-arylmaleimides rather than relying on fractional crystallization, we were also open to develop any new synthetic method that would equally necessitate a chromatographic separation as the final purification step. At the same time we were looking at the possibility of using $BrCCl_3$-PPh_3 as reagent to prepare amides and esters from carboxylic acids [27], and it was a natural continuation of this study to investigate whether the preparation of imides from carboxylic acids using $BrCCl_3$-PPh_3 would also be possible. Here, we report on the preparation of N-arylmaleimides **1** from maleanilic acids **4** with $BrCCl_3$-PPh_3 as reagent.



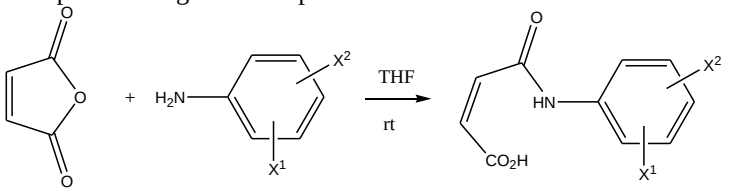
1

Fig. 1. Structure of *N*-arylmaleimide **1** as target structure.

II. Experimental

General. – General remarks. - Melting points were measured on a Stuart SMP 10 melting point apparatus and are uncorrected. Infrared spectra were measured with a Thermo/Nicolet Nexus 470 FT-IR ESP Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Varian 400 NMR spectrometer (^{1}H at 395.7 MHz, ^{13}C at 100.5 MHz). The assignments of the carbon signals were aided by DEPT 90 and DEPT 135 experiments (DEPT = Distortionless Enhancement by Polarisation Transfer). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer, and with an Agilent QTOF 6540 UHD. Column chromatography was performed on recycled silica gel (S, 0.063 mm – 0.1 mm, Riedel de Haen and Merck grade 9385). All silica gel is re-used upon thermal recycling [28]. CHN-analysis was performed on a LECO TruSpec Micro instrument. Analytical thin layer chromatography (TLC) was carried out on silica on TLC Alu foils from Fluka (with fluorescent indicator at λ = 254 nm). Triethylamine was dried over solid KOH and distilled.

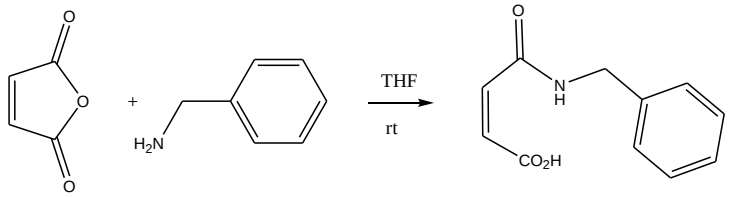
Chemicals. – Maleic anhydride (**2**) (Riedel de Haen), aniline (**3a**) (BDH), *o*-toluidine (**3c**) (Merck-Schuchardt), *p*-toluidine (**3d**) (Merck-Schuchardt), *p*-anisidine (**3e**) (Fluka), 2,4-dimethoxyaniline (**3f**) (Aldrich), 2,4-difluoroaniline (**3g**) (Aldrich), 2,6-difluoroaniline (**3h**) (Aldrich), 4-nitroaniline (**3i**) (Merck-Schuchardt), 2,6-dichloro-4-nitroaniline (Fluka), 4-chloroaniline (**3j**) (BDH), 4-cyanoaniline (4-aminobenzonitrile, **3k**) (Aldrich), benzylamine (**3L**) (Fluka), triphenylphosphine (PPh_3) (Aldrich), bromotrichloromethane (Aldrich) were acquired commercially and were used without any further purification. 4-Bromoaniline (**3b**) was prepared by bromination of aniline with bromine-dioxane complex in aniline [29]. Maleic acid monoarylamides (maleanilic acids) **4a**-**4k** were prepared by reaction of the corresponding anilines with maleic anhydride (**2**) in THF as solvent (rt, 24h, Scheme 1). Maleic acid benzylamide (**4L**) was synthesized from maleic anhydride (2) and benzylamine (**3L**) in THF (ambient temperature, 3h, Scheme 1). It was attempted to obtain maleic acid 2,6-dichloro-4-nitroanilide in the same way [30], i.e. by reaction of maleic anhydride (**2**) with 2,6-dichloro-4-nitroaniline in THF and in DMF at both rt and elevated temperatures (60 ˚C, up to 2 days), however, in our hands the reaction did not proceed to give the respective maleanilic acid.



2 **3** **4** (56 - 98%)

3a: X^1=X^2=H
3b: X^1=H; X^2=4-Br
3c: X^1=H; X^2=2-CH_3
3d: X^1=H; X^2=4-CH_3
3e: X^1=H; X^2=4-OCH_3
3f: X^1=2-OCH_3; X^2=5-OCH_3
3g: X^1=2-F; X^2=4-F
3h: X^1=2-F; X^2=6-F
3i: X^1=H; X^2=4-NO_2
3j: X^1=H; X^2=4-Cl
3k: X^1=H; X^2=4-CN

4a: X^1=X^2=H
4b: X^1=H; X^2=4-Br
4c: X^1=H; X^2=2-CH_3
4d: X^1=H; X^2=4-CH_3
4e: X^1=H; X^2=4-OCH_3
4f: X^1=2-OCH_3; X^2=5-OCH_3
4g: X^1=2-F; X^2=4-F
4h: X^1=2-F; X^2=6-F
4i: X^1=H; X^2=4-NO_2
4j: X^1=H; X^2=4-Cl
4k: X^1=H; X^2=4-CN



2 **3L** **4L** (93%)

Scheme 1. Known synthesis of maleanilic acids (**4**) from maleic anhydride (**2**) and anilines (**3**).

General procedure: *N*-Phenylmaleimide (1a). - A solution of triphenylphosphine (1.89 g, 7.21 mmol) and bromotrichloromethane ($BrCCl_3$, 1.56 g. 7.86 mmol) in dry CH_3CN (20 mL) was stirred at rt for 30 min., during which in turned dark yellow. Then, maleanilic acid (**4a**) (1.10 g, 5.76 mmol) was added, and the resulting mixture was stirred at 70˚C for 40 min. Thereafter, dry triethylamine (750 mg, 7.42 mmol) was added dropwise over 15 min., and the resulting mixture was stirred at 70˚C for 8h. The cooled mixture was added to water (50 mL), and the ensuing mixture was extracted with CH_2Cl_2 (3 X 35 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated *in vacuo*. The residue was subjected to rapid column chromatography on silica gel (CH_2Cl_2) to give **1a** (828 mg, 83%) a yellow, crystalline solid, mp. 88 – 89^{o}C (85 - 87 ^{o}C [Aldrich Catalogue 2005/2006]); ν_{max} (KBr/cm^{-1}) 3093, 1716, 1598, 1586, 1508, 1394, 1146, 1072, 1031,

1009, 832, 757, 695, 629, 586, 497, 466; δ_H (400 MHz, $CDCl_3$) 6.84 (2H, s), 7.31 – 7.39 (3H, m), 7.44 – 7.49 (2H, m); δ_C (100.5 MHz, $CDCl_3$) 126.1 (2C, CH), 128.0 (CH), 129.2 (2C, CH), 131.2 (C_{quat}), 134.2 (2C, CH), 169.5 (2C, C_{quat}, CO).

***N*-(4-Bromophenyl)maleimide (1b).** - pale yellow solid (1.59 g, 6.3 mmol, 58%), mp. 132 ^oC (Lit. 128 – 130 ^oC [31.32]); ν_{max} (KBr/cm^{-1}) 3090, 1721, 1492, 1400, 1386, 1149, 1066, 831, 707, 686, 585, 501; δ_H (400 MHz, $CDCl_3$) 6.85 (2H, s), 7.24 (2H, d, ^3J = 8.8 Hz), 7.58 (2H, d, ^3J = 8.8 Hz); δ_C (100.5 MHz, $CDCl_3$) 121.6 (C_{quat}), 127.4 (2C, CH), 130.2 (C_{quat}), 132.3 (2C, CH), 134.3 (2C, CH), 169.1 (2C, C_{quat}, NCO).

***N*-(2-Methylphenyl)maleimide (1c).** as a very pale yellow solid, mp. 76 – 78 ^oC (Lit. 76 – 77 ^oC [33]); ν_{max} (KBr/cm^{-1}) 3093, 2929, 1716, 1496, 1458, 1391, 1150, 1116, 1065, 83, 823, 768, 688, 630, 588, 475; δ_H (400 MHz, $CDCl_3$) 2.16 (3H, s, CH_3), 6.87 (2H, s), 7.11 (1H, d, ^3J = 7.6 Hz), 7.27 – 7.37 (3H, m); δ_C (100.5 MHz, $CDCl_3$) 17.9 (CH_3), 126.9 (CH), 128.7 (CH), 129.5 (CH), 129.9 (C_{quat}), 131.2 (CH), 134.4 (2C, CH), 136.5 (C_{quat}), 169.6 (C, C_{quat}, CO).

***N*-(4-Methylphenyl)maleimide (1d). –** a yellow crystalline solid, mp. 159 – 160^oC (Lit. mp. 158 – 160 ^oC [31,32]); ν_{max} (KBr/cm^{-1}) 3454 (w), 3093, 1708, 1518, 1408, 1391, 1153, 834, 710, 685, 503; δ_H (400 MHz, $CDCl_3$) 2.38 (3H, s, CH_3), 6.83 (2H, s), 7.19 (2H, d, ^3J = 8.8 Hz), 7.26 (2H, d, ^3J = 8.8 Hz); δ_C (100.5 MHz, $CDCl_3$) 21.2 (CH_3), 126.0 (2C, CH), 128.4 (C_{quat}), 129.8 (2C, CH), 134.2 (2C, CH), 138.1 (C_{quat}), 169.7 (2C, C_{quat}, CO); Found: C, 70.33; H, 4.95; N, 7.48%. Calcd. for $C_{11}H_9NO_2$ (187.19) C, 70.58; H, 4.85; N, 7.48%.

***N*-(4-Methoxyphenyl)maleimide (1e). – -** a yellow crystalline solid, mp. 157 – 158^oC (Lit. 157^oC [34]); ν_{max} (KBr/cm^{-1}) 3467, 3173, 3110, 3079, 3011, 2965, 2939, 2914, 2836, 1701, 1507, 1445, 1400, 1303, 1251, 1156, 1106, 1055, 828, 721, 687, 604, 582, 527, 431; δ_H (400 MHz, $CDCl_3$) 3.81 (3H, s, OCH_3), 6.82 (2H, s), 6.97 (2H, d, ^3J = 8.4 Hz), 7.21 (2H, d, ^3J = 8.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 55.5 (OCH_3), 114.5 (2C, CH), 123.7 (C_{quat}), 127.6 (2C, CH), 134.1 (2C, CH), 159.2 (C_{quat}), 169.8 (2C, C_{quat}, CO); Found: C, 65.02; H, 4.46; N, 6.89%. Calcd. for $C_{11}H_9NO_3$ (203.19) C, 65.65; H, 4.45; N, 6.79%.

***N*-(2,5-Dimethoxyphenyl)maleimide (1f). – -** a yellow crystalline solid, mp. 132 – 134 ^oC (Lit. 122 ^oC [35]); ν_{max} (KBr/cm^{-1}) 3117, 3007, 2964, 2942, 2832, 1708, 1515, 1455, 1388, 1284, 1232, 1193, 1155, 1043, 1014, 822, 724, 692; δ_H (400 MHz, $CDCl_3$) 3.73 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 6.73 (1H, bs), 6.82 (2H, bs), 6.93 (2H, s); δ_C (100.5 MHz, $CDCl_3$) 55.8 (OCH_3), 56.3 (OCH_3), 113.1 (CH), 115.7 (CH), 115.8 (CH), 120.1 (C_{quat}), 134.4 (2C, CH), 149.6 (C_{quat}), 153.5 (C_{quat}), 169.6 (2C, C_{quat}, CO). Found: C, 61.62; H, 4.84; N, 6.01%. Calcd. for $C_{12}H_{11}NO_4$ (203.19) C, 61.80; H, 4.75; H, 6.01%.

***N*-(2,4-Difluorophenyl)maleimide (1g). –**as a colorless, crystalline solid, mp. 92 ^oC; (Lit. 92 $^\circ C$ [36]); ν_{max} (KBr/cm^{-1}) 3097, 1719, 1519, 1414, 1397, 1275, 1146, 975, 865, 831, 719, 689, 600, 439; δ_H (400 MHz, $CDCl_3$) 6.91 (2H, s), 6.97 – 7.02 (2H, m), 7.23 – 7.29 (1H, m); δ_C (100.5 MHz, $CDCl_3$) 105.3 (CH, dd, $^2J_{CF}$ 26.9 Hz, $^2J_{CF}$ 23.9 Hz), 112.0 (CH, dd, $^2J_{CF}$ 22.4 Hz, $^4J_{CF}$ 3.7 Hz), 114.9 (C_{quat}, dd, $^2J_{CF}$ 13.5 Hz, $^4J_{CF}$ 3.7 Hz), 130.7 (CH, dd, $^3J_{CF}$ 9.6 Hz, $^3J_{CF}$ 1.6 Hz), 134.7 (2C, CH), 158.1 (dd, $^1J_{CF}$ 255.0 Hz, $^3J_{CF}$ 12.8 Hz), 162.9 (C_{quat}, $^1J_{CF}$ 251.4 Hz, $^3J_{CF}$ 11.3 Hz), 168.6 (C_{quat}, CO).

***N*-(2,6-Difluorophenyl)maleimide** (**1h**). –a colorless, crystalline solid, mp. 108 ^oC (Lit. 91-93 ^oC [37]); ν_{max} (KBr/cm^{-1}) 3492, 3123, 1724, 1596, 1514, 1475, 1387, 1243, 1220, 1161, 1136, 1048, 990, 825, 781, 691, 584; δ_H (400 MHz, $CDCl_3$) 6.92 (2H, s), 7.04 (2H, m), 7.40 (1H, m); δ_C (100.5 MHz, $CDCl_3$) 108.4 (dd, C_{quat}, $^2J_{CF}$ = 16.0 Hz, $^2J_{CF}$ = 16.0 Hz), 112.1 (2C, CH, md, $^2J_{CF}$ = 18.6 Hz), 131.0 (2C, CH, dd, $^3J_{CF}$ = 9.7 Hz, $^3J_{CF}$ = 9.7 Hz), 135.0 (2C, CH), 158.9 (2C, C_{quat}, dd, $^1J_{CF}$ = 253.0 Hz, $^4J_{CF}$ = 3.7 Hz), 169.0 (C_{quat}, CO).

***N*-(4-Nitrophenyl)maleimide** (**1i**). – as a solid, mp. 168 $^\circ C$ (Lit. 168-170 $^\circ C$ [38]); ν_{max} (KBr/cm^{-1}) 3120, 3105, 1717, 1522, 1505, 1387, 1349, 1145, 1058, 849, 826, 699; δ_H (400 MHz, DMSO-d^6) 7.28 (2H, s), 7.70 (2H, d, ^3J = 9.0 Hz), 8.37 (2H, d, ^3J = 9.0 Hz); δ_C (100.5 MHz, DMSO-d^6) 124.2 (2C, CH), 126.7 (2C, CH), 135.0 (2C, CH), 137.5 (C_{quat}), 145.7 (C_{quat}), 169.1 (2C, C_{quat}, CO);

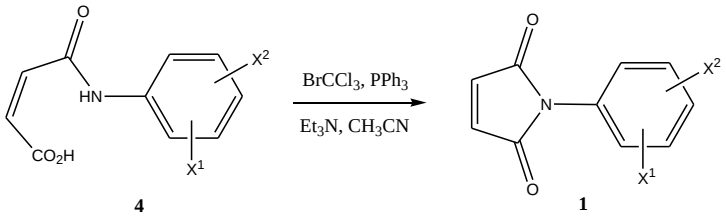
***N*-(4-Chlorophenyl)maleimide** (**1j**). – pale yellow, crystalline solid, mp. 115 $^\circ C$ (Lit. 114-115 °C [32]); ν_{max} (KBr/cm^{-1}) 3085, 1713, 1498, 1462, 1388, 1149, 1097, 1070, 836, 709, 685, 586, 504, 418; δ_H (400 MHz, $CDCl_3$) 6.86 (s, 2H), 7.25 (d, 2H, ^3J = 8.4 Hz), 7.59 (d, 2H, ^3J = 8.4 Hz); δ_C (100.5 MHz, $CDCl_3$) 119.2, 125.0, 128.1, 130.0, 132.1, 169.8.

N-(4-Cyanophenyl)maleimide (**1k**). – colorless solid; mp. 128 ˚C (Lit. 129 – 130 °C [38]); ν_{max} (KBr/cm^{-1}) 3168, 3103, 3093, 2238, 1726, 1515, 1393, 1375, 1145, 843, 830, 691, 589, 543; δ_H (400 MHz, $CDCl_3$) 6.85 (2H, s), 7.52 (2H, d, ^3J = 8.8 Hz), 7.67 (2H, d, ^3J = 8.8 Hz), 7.40 (1H, m); δ_C (100.5 MHz, $CDCl_3$) 111.0, 118.8, 125.4, 132.8, 134.4, 135.5, 168.7.

III. Results and Discussion

Synthesis.

The reaction of alkanols to alkyl chlorides with CCl_4-PPh_3 is called the Appel reaction [39]. CCl_4-PPh_3 can also be used as a dehydrating agent, eg., to furnish alkyl nitriles from alkanamides and thus is also useful in the preparation of esters and amides from the corresponding acids [39]. Tetrachloromethane (CCl_4) is an ozone depletory; therefore it is being phased out. We have looked at bromotrichloromethane ($BrCCl_3$) as a substitute for CCl_4. $BrCCl_3$ has a higher boiling point than CCl_4 (105 ˚C vs. 76.7 ˚C), but also has a larger dipole moment (0.40 D), which reduces the average residence time of the compound in the atmosphere, once released. The combination $BrCCl_3$-PPh_3 can replace CCl_4-PPh_3 in many reactions such as in the dehydration of amides and aldoximes to nitriles [40] and in the esterification and amidation of carboxylic acids [27]. The actual transformations may in fact take a number of simultaneously running mechanisms. Thus, the reaction of carboxylic acids with CCl_4 or $BrCCl_3$–PPh_3 can initially lead acyl halides, which partly can convert to acid anhydrides under the conditions. Both acyl halides and anhydrides can react with the subsequently added amines or alkanols to amides and esters, respectively. As the amidation of carboxylic acids proceeds facilely with $BrCCl_3$-PPh_3 [27], even with the less nucleophilic anilines [41], it was envisaged that under the conditions perhaps even an amide function would be nucleophilic enough to undergo an intramolecular reaction with an activated carboxyl function to the corresponding imide, such as in our case the amide function of a maleanilic acid.



4

4a: X^1=X^2=H
4b: X^1=H; X^2=4-Br
4c: X^1=H; X^2=2-CH_3
4d: X^1=H; X^2=4-CH_3
4e: X^1=H; X^2=4-OCH_3
4f: X^1=2-OCH_3; X^2=5-OCH_3
4g: X^1=2-F; X^2=4-F
4h: X^1=2-F; X^2=6-F
4i: X^1=H; X^2=4-NO_2
4j: X^1=H; X^2=4-Cl
4k: X^1=H; X^2=4-CN

1

1a: X^1=X^2=H (83%)
1b: X^1=H; X^2=4-Br (79%)
1c: X^1=H; X^2=2-CH_3 (74%)
1d: X^1=H; X^2=4-CH_3 (78%)
1e: X^1=H; X^2=4-OCH_3 (81%)
1f: X^1=2-OCH_3; X^2=5-OCH_3 (65%)
1g: X^1=2-F; X^2=4-F (80%)
1h: X^1=2-F; X^2=6-F (79%)
1i: X^1=H; X^2=4-NO_2 (34%)
1j: X^1=H; X^2=4-Cl (77%)
1k: X^1=H; X^2=4-CN (84%)

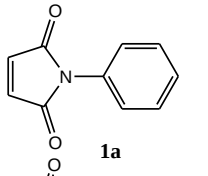
Scheme 2. Preparation of *N*-arylmaleimides **1** from maleanilic acids **4** with $BrCCl_3$/PPh_3 as reagent.

First, the maleanilic acids had to be prepared by the reaction of anilines with maleic anhydride. For the most part, anilines readily react with maleic anhydride under ring opening to maleic acid monoarylamides (maleanilic acids, **4**) at room temperature. The more nucleophilic benzylamine (**3L**) undergoes the reaction exothermally. Although described in the literature [30], the reaction of 2,6-dichloro-4-nitroaniline with maleic anhydride posed a problem for us, no reaction occurring in either THF or DMF at rt (12h), and no reaction occurring in DMF at 67 °C (12h). This may be due to the withdrawing character of the substituents, making the aniline nitrogen little nucleophilic. However, it must be noted that 2,6-difluoroaniline does react readily under the conditions, so that steric hindrance of the chloro substituents in 2,6-dichloro-4-nitroaniline may also contribute.

For the Appel reaction, acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) are usually the solvents of choice. Because of the sparing solubility of maleanilic acids in CH_2Cl_2, CH_3CN was used as solvent. Previously, we had realized that acids can be converted to esters even in the absence of a HX-scavenging base. When running the reaction of maleanilic acids in CH_3CN with $BrCCl_3$-PPh_3 in the absence of a base, *N*-arylmaleimides are formed, but the reactions do not complete. Therefore, triethylamine as base has to be introduced dropwise as the reaction proceeds. Overall, the transformation of maleanilic acids with $BrCCl_3$-PPh_3 in the presence of triethylamine leads to *N*-arylmaleimides in acceptable yields (Scheme 2). The products were purified by rapid column chromatography on silica gel. It must be noted that the maleamic acid **4L** did not cyclize to the corresponding *N*-benzylmaleimide under the conditions above.

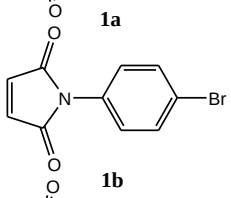
UV-VIS spectroscopy.

As N-arylmaleimides are important enes in cycloaddition reactions and are used as radical initiators for the preparation of thermally or photolytically cured polymers [42], there has always been an interest to probe the higher-lying molecular orbitals of the molecules. This can be done, in part, by UV-VIS spectroscopy. A larger number of authors have reported on the spectroscopic behavior of maleimide and its derivatives [43,44], including the computational analysis of the photochemical transitions involved [45-48]. One of the first authors who examined the nature of the UV-VIS absorption bands is T. Matsuo, who investigated the spectra of *N*-phenylmaleimide (**1a**), *N*-(4-methoxyphenyl)maleimide (**1e**), *N*-(4-chlorophenyl)maleimide (**1j**), and *N*-(4-tolyl)maleimide (**1d**) in addition to *N*-alkylmaleimide as well as *N*-maleimide itself [49]. Also, C. W. Miller et al. tabulated the UV-VIS spectra of a number of other 2- and 4–substituted *N*-phenylmaleimides [42]. Tables 1 and 2, below, show the maxima in the UV spectra of the prepared *N*-arylmaleimides **1a-1k** as measured by the authors. Many *N*-phenylmaleimides **1** were noted, as in the reported in the literature, to have two main absorption bands between λ = 350 nm and λ = 260 nm, where the higher energy absorption band shows less solvent effect than the longest wavelength absorption band [49]. The absorption at the longest wavelength has been noted to be an n → π* transition of the carbonyl groups [49] of the imide with some perturbation from a π → π* transition. Intensity values of the band are between ε = 250 for **1h** in pentane and ε = 550 for **1j** in acetonitrile, with most other values between ε = 350 and ε = 450.



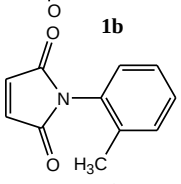
1a

CH_2Cl_2: λ = 315 nm 260 nm
CH_3CN: λ = 305 nm 260 nm
EtOH: λ = 281.5 nm (broad)
Pentane: λ = 315 nm 260 nm



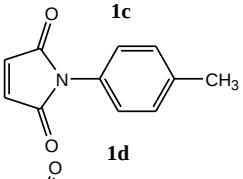
1b

CH_2Cl_2: λ = 315 nm 270 nm
CH_3CN: λ = 310 nm 267 nm
EtOH: λ = 312 nm 268 nm
Pentane: λ = 325 nm 271 nm (278.5 nm)



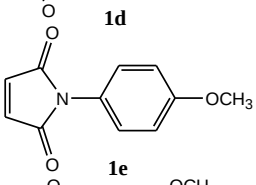
1c

CH_2Cl_2: λ = 295 nm 265 nm
CH_3CN:λ = 295 nm 270 nm
EtOH: λ = 295 nm 265 nm
Pentane: λ = 295 nm 265 nm



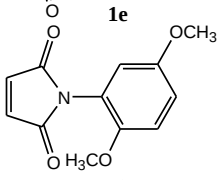
1d

CH_2Cl_2: λ = 315 nm 265 nm
CH_3CN: λ = 308 nm 267 nm
EtOH: λ = 309 nm 264 nm
Pentane: λ = 320 nm 264 nm



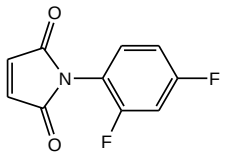
1e

CH_2Cl_2: λ = 330 nm 275 nm
CH_3CN: λ = 325 nm 275 nm
EtOH: λ = 341 nm 275 nm
Pentane: λ = 345 nm 275 nm



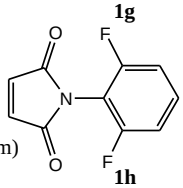
1f

CH_2Cl_2: λ = 295 nm
CH_3CN:λ = 295 nm
EtOH:λ = 295 nm
Pentane: λ = 295 nm



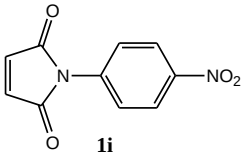
1g

CH_2Cl_2: λ = 300 nm 265 nm
CH_3CN: λ = 295 nm 265 nm
EtOH: λ = 295 nm 265 nm
Pentane: λ = 290 nm 265 nm



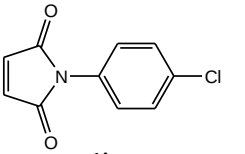
1h

CH_2Cl_2: λ = 290 nm 260 nm
CH_3CN: λ = 280 nm 260 nm
EtOH: λ = 282 nm 260 nm
Pentane: λ = 281 nm 260 nm



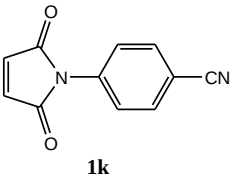
1i

CH_2Cl_2: λ = 285 nm
CH_3CN: λ = 285 nm
EtOH: λ = 280 nm
Pentane: λ = 275 nm



1j

CH_2Cl_2: λ = 315 nm 270 nm
CH_3CN: λ = 305 nm 270 nm
EtOH: λ = 312 nm 270 nm
Pentane: λ = 315 nm 270 nm (278.5 nm)



1k

CH_2Cl_2: λ = 310 nm 245 nm
CH_3CN: λ = 305 nm 245 nm
EtOH: λ = 305 nm 244 nm (260 nm)
Pentane: λ = 315 nm 245 nm

Table 1. Longest wavelength absorptions of the *N*-arylmaleimides **1**

The longest wavelength absorption in 2-substituted *N*-arylmaleimides such as in **1c**, **1f**, **1g**, and **1h** is shifted to higher energy as compared to the 4-substituted systems. This is due to the higher energy of the rotational barrier of N-C between the phenyl group and maleimide moiety, which forces the 2-substituted molecules out of planarity. This has been reported in the literature for other 2-substituted *N*-arylmaleimides, also [50]. There is not a clear-cut dependence of the energy of the longest wavelength absorption on the electronic character of the *p*-substituent of aryl group. Thus, non-substituted **1a** and chloro-substituted **1j** essentially show the band at the same wavelength in most solvents. Only for the 4-methoxy-substituted **1e** does one find a shift of the transition to higher wavelength. Then, again substituents that have an appreciable electronic interaction with

the phenyl group such as in **1i**, **1k** and **1f** may lead to HOMO and LUMO being of a different character than in **1b** or **1j**. This is currently under investigation in our group.

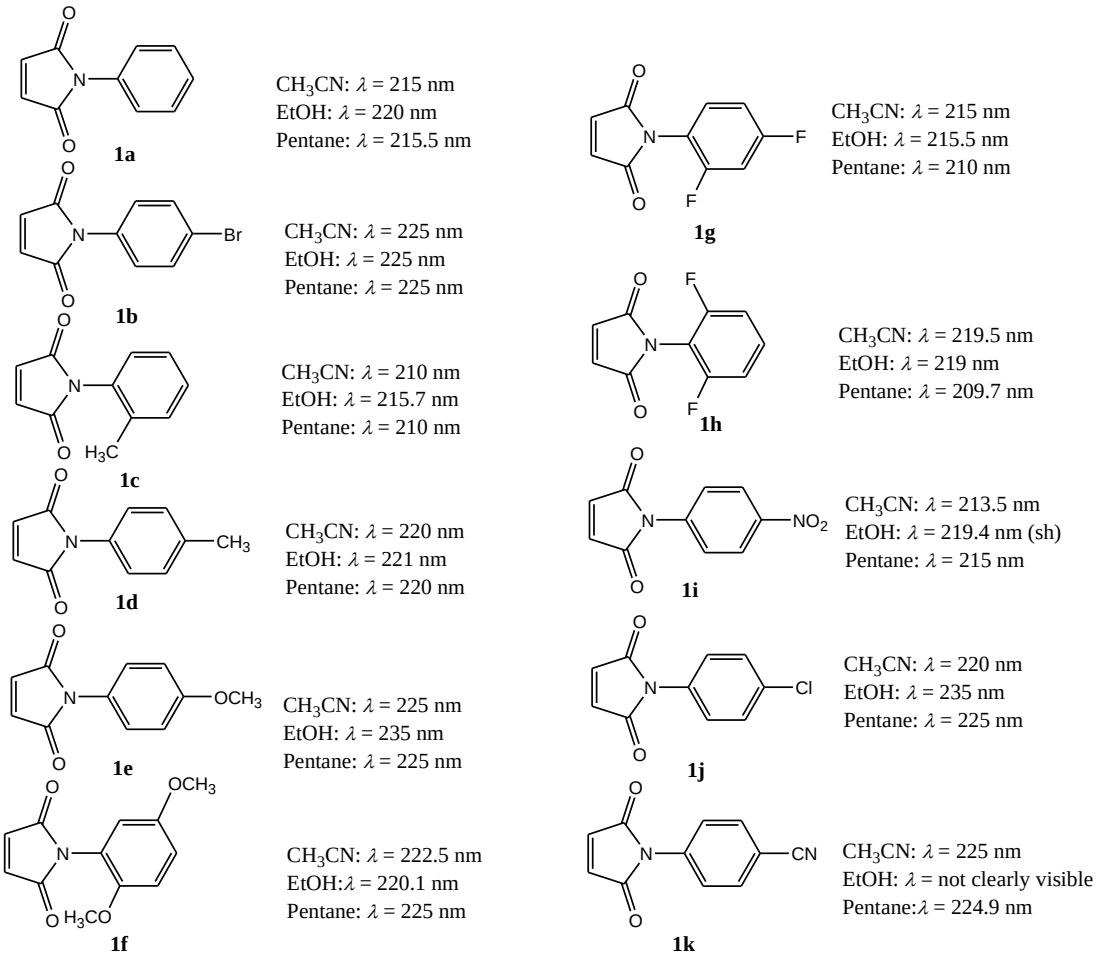


Table 2. Shortest wavelength absorption measured with UV-VIS spectroscopy for *N*-arylmaleimides **1** within the solvent window.

IV. Conclusion

A number of substituted *N*-arylmaleimides **1** were prepared from the respective maleanilic acids by the action of the Appel-type reagent triphenylphosphine (PPh_3) and bromotrichloromethane ($BrCCl_3$) in acetonitrile, circumventing the CO_2 production occurring during work-up when using the established synthesis of *N*-arylmaleimides **1** with CH_3CO_2H/NaOAc. The UV-spectra of the *N*-arylmaleimides **1** were recorded in different solvents.

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