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SYNTHESIS OF N-(FLUORO PHENYL) MALEAMIC ACIDS AND N-(FLUORO PHENYL) MALEIMIDES

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SUMMARY

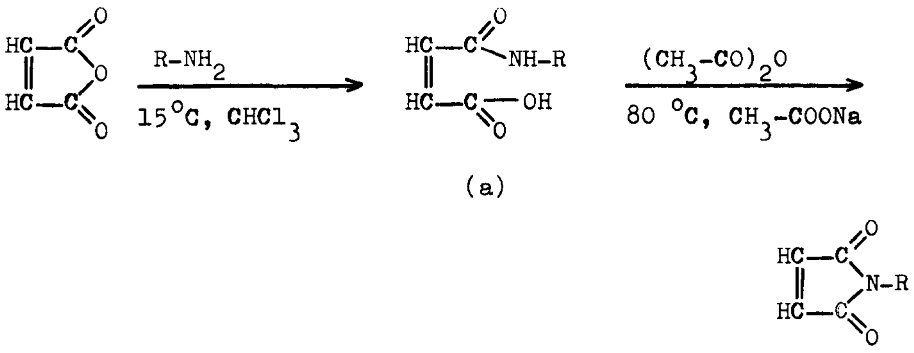
A series of seven N-(fluoro phenyl) maleamic acids and their N-(fluoro phenyl) maleimides were prepared by the reaction of fluoro phenyl amines (o-, m-, and p-fluoro, 2.4-, 2.5-difluoro, 2.3.5.6-tetrafluoro and 2.3.4.5.6-pentafluoro anilines) with maleic anhydride according to substantial modifications made to the reaction conditions used by Searle for the preparation of normal N-aryl maleimides.

INTRODUCTION

In a previous paper [1] we described the preparation of a series of N-(n-alkyl) and N-(phenyl n-alkyl) maleamic acids and their corresponding N-(n-alkyl) and N-(phenyl n-alkyl) maleimides. In this paper, a series of N-(fluoro phenyl) maleimides were prepared as well as their corresponding N-maleamic acids. The preparation of these compounds was undertaken because these substances were needed as intermediates in the preparation of a series of high molecular weight compounds [2] . Therefore, the synthesis of N-(fluoro phenyl) maleimides seemed to be of interest.

To date several synthetic methods have been applied both to N-(n-alkyl) and N-(aryl) maleimides. They are based on the thermal dehydration of the corresponding N-maleamic acids [3][4] or alternatively in the treatment of the solutions of these same acids with phosphorous pentoxide [5] [6] . These methods need to work at a high temperature and the resulting N-maleimides are not only obtained with very low yields (10-25 %), but also they are accompanied by a series of secondary products which are difficult to separate. Simultaneously, due to the formation of a considerable quantity of polymeric products, is produced a loss of monomeric N-maleimide. Another preparation method uses the reaction of maleic anhydride and the primary amines at temperatures over 160 °C using thionyl chloride as catalyst [4] ; likewise together with the N-maleimides, other undesirable secondary products are formed. There are also other authors who have introduced very simple variations which are not substantial over the general ones already mentioned. It should be pointed out that Lukeš and Pergál [7] start from maleic acid and the corresponding primary amine and then through a series of intermediate steps obtain N-maleimides.

In the current patent literature, there exist a general method of obtaining N-aryl maleimides [8] which leads to very high yields, however the reactions described in the aforementioned patent are incomplete and the products obtained have not been characterized. The Searle reaction [8] takes place as from maleic anhydride and an aromatic primary amine, obtaining the corresponding N-aryl maleamic acid (a) as an intermediate compound, which subsequently, by cycling through the loss of one molecule of water , leads to the N-aryl maleimide (b), without the formation of any other product. The course of reaction is as follows,



(a)

(b)

Therefore, the main object of the present work has been the preparation of new N-aryl maleimides, not only with very high yields, but also excluding secondary products, which undoubtedly improve the purity of the basic products. Consequently, characterization has been dealt with and specially the determination of characteristic chemical constants and purity, since these are necessary for the subsequent polymerization and characterization of the polymers, very specially when the method of polymerization with ^{60}Co gamma radiation is used, since the impurities, especially in the case of their existence in the form of N-maleamic acids, not only reduce polymer yields and enable the formation of copolymers, but at times can even become real inhibitors of the polymerization process [9].

The presentation of the material of the current work has been subdivided, for convenience, according to the types of compounds involved. In the first place, the N-(fluoro phenyl) maleamic acid derivatives of o-, m-, p-fluoro, 2.4-, 2.5-difluoro, 2.3.5.6-tetrafluoro and 2.3.4.5.6-pentafluoro anilines are presented and in the second place, their corresponding N-(fluoro phenyl) maleimides.

Apart from using these substances as monomers or comonomers in copolymerization, they can also prove worthwhile for their possible applications outside the macromolecular field. Thus some other unfluorinated N-maleimides have been found to have applications such as detergent and lubricating oil additives [10] , as crosslinking agents of different types of polymers and rubbers [11][12] , as well as for a wide and varied field of industrial, biological and pharmacological uses [13].

EXPERIMENTAL

Melting points have been determined by means of a differential scanning calorimetric cell DSC (Du Pont, Wilmington, Delaware) which has a differential thermal analysis equipment Du Pont 900 as control and recording unit. Experimental working conditions and other details have been carefully described previously [1] . The elemental analysis was carried out with an elemental analyzer Perkin-Elmer, model 240. The IR absorption spectra were recorded with a double beam spectrograph, Perkin-Elmer, model 457 using the KBr disc technique (2-3 mg/100 mg KBr). The nuclear magnetic resonance spectra (^{1}H NMR) were recorded out at 37 °C with a 60 MHz Perkin-Elmer spectrometer, model R 10 in hexadeuterated dimethyl sulphoxide (Me_2SO-d_6) for N-maleamic acids and carbon tetrachloride (CCl_4) for N-maleimides, using in both cases tetramethylsilane (TMS)as an internal standard (0.5 %). Ultraviolet absorption spectra were obtained for N-maleamic acids and N-maleimides using ethanol (EtOH) or dioxane solution at 25 °C with a Perkin-Elmer, model 350 UV spectrometer and 1 cm quartz cells. The homogeneity of N-maleimides was carried out by means of thin layer chromatography (TLC) using benzene-ethyl acetate (85:15) for elution and silica gel plates of 60 PF_{354} type (Merck, A.G.). The spots were located by exposing the dried plates in an ultraviolet lamp (254 and 350 nm). Solubilities of N-(fluoro phenyl) maleamic acids and their N-maleimides have been determined in 20 ml test tubes. In each case, a mixture of the compound (100 mg) as finely divided particles in 10 ml of solvent was maintained at 25 °C for 24 hr. The mixture was then observed. The results are summarized as follows: N-(fluoro phenyl) maleamic acids are soluble in dioxane, dimethyl sulphoxide, N,N-dimethyl formamide, o-chlorophenol, pyridine and ethanol and insoluble in cyclohexane, benzene and toluene. N-(fluoro phenyl) maleimides are soluble in carbon tetrachloride, dioxane, ethanol, m-cresol, o-clorophenol, N,N-dimethyl formamide, dimethyl sulphoxide and toluene and insoluble in n-hexane.

All of the N-(fluoro phenyl) maleamic acids and N-(fluoro phenyl) maleimides described herein were prepared from the appropiate amines. The synthesis and characteristics of these are given below. Fluoro phenyl anilines were analytical grade reagents (obtained from Fluka, A.G., Switzerland). All solvents used were of reagent grade and were purified by standard procedures. All reactions were carried out under a nitrogen atmosphere.

RESULTS AND DISCUSSION

N-(fluoro phenyl) maleamic acids

N-(2-fluoro phenyl) maleamic acid (I). General procedure

Pulverized maleic anhydride (C.Erba, S.p.A.)(24.5 g, 0.25 moles) and chloroform (Merck, A.G.)(125 ml) were placed in a 250 ml round-bottomed five-necked flask. The flask was fitted with a mechanical stirrer, a condenser, a dropping funnel, a thermometer and a gas inlet tube. The suspension was stirred vigorously and a solution of ortho-fluoro aniline (27.75 g, 0.25 moles) in chloroform (100 ml) was added slowly through the dropping funnel; the first drops turned yellow on contacting the suspension. The temperature was kept at 15-20 °C by means of a water-ice bath. After the addition was half complete more chloroform (100 ml) was added, to make the suspension thinner since the N-(2-fluoro phenyl) maleamic acid formed is insoluble in the reaction mixture. Once the addition of the amine solution has been completed, stirring was continued for a further half hour. The final product was a yellow dusty solid. It was filtered off and dried in vacuo at 40 °C; the yield was 46 g crude N-(2-fluoro phenyl) maleamic acid (88.1 %). The crude compound was recrystallized from ethanol-water (1:1), gave rectangular prismatic crystals of melting point, 163 °C. Analysis. Found: C, 57.57; H, 3.85; N, 6.89. $C_{10}H_8O_3NF$ requires C, 57.51; H, 3.82; N, 6.69. Several characteristic types of bands occur in the infrared spectra (IR) of both N-(fluoro phenyl) maleamic acids and N-(fluoro phenyl) maleimides. A classification of the various types of bands will be given. We therefore define the following band classes. The acid group can be assigned to two frequencies which appear with reasonably uniformity 1710 cm^{-1} $\nu(C{=}O)$ and 975 cm^{-1} $\gamma(OH)$. Bands at 3260 cm^{-1} $\nu(NH)$, 1615 cm^{-1} (band I) and 1550 cm^{-1} (band II) are due to secondary amid groups. The aromatic ring produces bands at 1580 cm^{-1} $\nu(C{=}C)$ and 1485 cm^{-1} $\nu(C{=}C)$; the characteristic features of 1.2 disubstitution appear at 865 cm^{-1} and 760 cm^{-1} and at 1235 cm^{-1} $\nu(C\text{-}F)$. The ethylenic double bond is confirmed by absorption bands appearing at 855 cm^{-1}, dues to an out-of-plane deformation vibration of C-H in HC=CH conjugated with C=O groups and at 3090 cm^{-1} $\nu(CH)$. NMR ($Me_2SO\text{-}d_6$) shows a wide and diffuse chemical shift at $-2.00\,\tau$ (ppm) It can be assigned to the hydrogen of the acid group. This is confirmed by a comparison of the spectrum with that of the methylay derivative since the signal shows a general resemblance to that of the amidic group. The acidic proton is confirmed by adding diazomethane (0.2 ml) to 50 mg of (I). The NMR spectrum of this compound does not show the characteristic signal at $-2.00\,\tau$ (ppm), confirming the presence of the acidic hydrogen in the original compound (I) and establishing undoubtedly the presence of this class of chemical shift for all the compounds to which we have assigned such structure. At -0.35τ (ppm) appears a singlet due to the imidic hydrogen and a multiplet at $2.0-2.8\,\tau$ (ppm) and a quartet at $3.55\,\tau$ (ppm) due to hydrogen from aromatic rings and ethylenic protons , respectively. Furthermore, the integration corresponds to the protons according to that of the molecule under consideration. UV (ethanol) shows a maximum ($\lambda = 282$ nm; $\epsilon = 6950$) and a minimum ($\lambda = 252$ nm; $\epsilon = 5200$).

N-(3-fluoro phenyl) maleamic acid

This material was prepared by a method similar to that used for (I). Maleic anhydride (24.5 g; 0.25 moles) was dissolved in m-fluoro aniline (27.75 g; 0.25 moles) in chloroform (500 ml). The precipitated crude solid (49.6 g) of N-(3-fluoro phenyl) maleamic acid (95.0 %) on recrystallization from ethanol-water (1:2) gave a product as white solid, m.p. 195 °C. Analysis. Found: C, 57.35; H, 3.79; N, 6.48. $C_{10}H_8O_3NF$ requires C, 57.41; H, 3.82; N, 6.69. IR (KBr), 3270 cm^{-1} ν(NH), 3100 cm^{-1} ν(CH), 1715 cm^{-1} ν(C=O), 1625 cm^{-1} (band I), 1600 cm^{-1} ν(C=C), 1545 cm^{-1} (band II), 1490 cm^{-1} ν(C=C), 1255 cm^{-1} ν(C-F), 980 cm^{-1} γ(OH), 855 cm^{-1} γ(C-H), 780 cm^{-1} and 675 cm^{-1} (1.3-substitution). NMR: $-2.75\,\tau$ (ppm) (acid, wide chemical shift), $-0.50\,\tau$ (ppm) (amidic, singlet), $2.2-2.6\,\tau$ (ppm) (multiplet, aromatic), $3.55\,\tau$ (ppm) (ethylenic, quartet). UV (ethanol), maximum ($\lambda = 284$ nm; $\epsilon = 7230$) and a minimum ($\lambda = 253$ nm; $\epsilon = 5380$).

N-(4-fluoro phenyl) maleamic acid

As in similar reaction to (I), maleic anhydride (49 g; 0.5 moles) and p-fluoro aniline (55.5 g ; 0.5 moles) in 600 ml of chloroform, reacted to give 99.5 g of N-(4-fluoro phenyl) maleamic acid (95.5 %). This was isolated and recrystallized from ethanol giving white needles, m.p. 210 °C. Analysis. Found: C, 57.32; H, 3.77; N, 6.85. $C_{10}H_8\,O_3$ NF requires C, 57.41; H, 3.82;

N, 6.69. IR (KBr), 3240 cm^{-1} ν(NH), 3090 cm^{-1} ν(CH), 1700 cm^{-1} ν(C=O), 1630 cm^{-1} (band I), 1610 cm^{-1} ν(C=C), 1550 cm^{-1} (band II), 1490 cm^{-1} ν(C=C), 1230 cm^{-1} ν(C-F), 980 cm^{-1} γ(OH), 855 cm^{-1} γ(CH), 830 cm^{-1} (1.4-substitution). NMR: -2.90 τ (ppm)(acid, wide signal), -0.45 τ (ppm)(amidic, singlet), 2.35-2.85 τ (ppm) (aromatic, multiplet), 3.55 τ (ppm) (ethylenic, quartet). UV (dioxane), maximum (λ = 282 nm; ε = 6680) minimum (λ = 253 nm; ε = 4880) and shoulder (λ = 302 nm; ε = 5460)

N-(2.4-difluoro phenyl) maleamic acid

In a similar reaction to (I), maleic anhydride (0.38 g; 0.039 moles), 2.4-difluoro aniline (5 g ; 0.039 moles), in chloroform (150 ml) gave 8.1 g of N-(2.4-difluoro phenyl) maleamic acid (92.0 %). Recrystallization from ethanol converted this product to white needles, m.p. 197 °C. Analysis. Found: C, 53.00; H, 3.03; N, 6.31. $C_{10}H_7O_3NF_2$ requires C, 52.86; H, 3.08; N, 6.16. IR (KBr), 3230 cm^{-1} ν(NH), 3070 cm^{-1} ν(CH), 1710 cm^{-1} ν(C=O), 1635 cm^{-1} (band I), 1550 cm^{-1} (band II), 1510 cm^{-1} ν(C=C), 1270 cm^{-1} ν(C-F), 970 cm^{-1} γ(OH), 855 cm^{-1} γ(CH), 810 cm^{-1} (1.2.4-trisubstitution). NMR: -2.40 τ (ppm)(acid, wide chemical signal), -0.25 τ (ppm)(amidic, singlet), 2.0-2.75 τ (ppm) (aromatic, multiplet), 3.55 τ (ppm)(ethylenic, quartet). UV (ethanol), maximum (λ = 276 nm; ε = 5830) and a minimum (λ = 251 nm; ε = 4710).

N-(2.5-difluoro phenyl) maleamic acid

This compound was synthesized by the method given for (I). Maleic anhydride (3.8 g; 0.038 moles) was dissolved in a solution of 2.5-difluoro aniline (5 g; 0.038 moles) in chloroform (125 ml); giving 7.5 g (85.8 %) of a solid mass which on recrystallization from ethanol-water (1:1) gave rectangular prismatic crystals, melting at 170 °C. Analysis. Found: C, 52.67; H, 3.04; N, 6.39. $C_{10}H_7O_3NF_2$ requires C, 52.86; H, 3.08; N, 6.16. IR (KBr), 3070 cm^{-1}

ν(CH), 1695 cm^{-1} ν(C=O), 1630 cm^{-1} (band I), 1570 cm^{-1} (band II), 1495 cm^{-1} ν(C=C), 1200 cm^{-1} ν(C-F), 970 cm^{-1} γ(OH), 870 cm^{-1} (1.2.5-trisubstitution), 850 cm^{-1} γ(CH), 810 cm^{-1} (1.2.5-trisubstitution). NMR: -2.30 τ (ppm)(acid, wide chemical shift), -0.45 τ (ppm)(amidic, singlet), 2.0-2.75 τ (ppm)(aromatics, multiplet), 3.55 τ (ppm)(ethylenic, quartet). UV (ethanol), maximum (λ = 286 nm; ϵ = 7380) and a minimum (λ = 275 nm; ϵ = 4590).

N-(2.3.5.6-tetrafluoro phenyl) maleamic acid

A mixture prepared by dropping stepwise 2.3.5.6-tetrafluoro aniline (2.5 g ; 0.015 moles) dissolved in toluene (40 ml) to a solution of maleic anhydride (1.47 g; 0.015 moles) in 80 ml of toluene at 105 °C, was stirred for 8 hr. After cooling at room temperature the reaction mixture was distilled in vacuo. The compound separated as a waxy solid. The yield was 65.5 %. The product N-(2.3.5.6-tetrafluoro phenyl) maleamic acid after recrystallization from water lamellar crystals were obtained which melted at 121 °C. Analysis. Found : C, 45.57; H, 1.85; N, 5.56. $C_{10}H_5O_3NF_4$ requires C, 45.62; H, 1.90; N, 5.33. IR (KBr), 3250 cm^{-1} ν(NH), 3070 cm^{-1} ν(CH), 1710 cm^{-1} ν(C=O), 1635 cm^{-1} (band I), 1545 cm^{-1} (band II), 1500 cm^{-1} ν(C=C), 1260 cm^{-1} ν(C-F), 995 cm^{-1} γ(OH), 840 cm^{-1} γ(CH). NMR: -0.50 τ (ppm)(amidic, singlet), 2.15 τ (ppm)(aromatic, multiplet), 3.55 τ (ethylenic, quartet). UV (ethanol), shoulder (λ = 267 nm; ϵ = 4240).

N-(pentafluoro phenyl) maleamic acid

This compound was prepared by the procedure given for the above analog. A mixture of 1.32 g (0.014 moles), 100 ml of toluene, and 2.5 g (0.014 moles) of pentafluoro aniline was heated at 105 °C under vigourously stirring for 8 hours. A yield of 2.51 g (65.7 %) was obtained. The product was recrystallized from water giving white crystals which melted at 106.5 °C. Analysis. Found: C, 43.00; H, 1.36; N, 5.15. $C_{10}H_4O_3NF_5$ requires C, 42.70; H, 1.42; N, 4.98. IR (KBr), 3220 cm^{-1} ν(NH), 3095 cm^{-1} ν(CH), 1705 cm^{-1} ν(C=O), 1625 cm^{-1} (band I), 1595 cm^{-1} ν(C=C), 1550 cm^{-1} (band II), 1500 cm^{-1} ν(C=C), 1270 cm^{-1} ν(C-F), 970 cm^{-1} γ(OH), 855 cm^{-1} γ(C-H). NMR: -0.55 τ (ppm)(amidic, singlet), 3.55 τ (ppm)(ethylenic, quartet). UV (ethanol), shoulders (λ = 227 nm; ϵ = 5220 and λ = 260 nm; ϵ = 1880).

N-(fluoro phenyl) maleimides

N-(2-fluoro phenyl) maleimide. (General procedure) (II)

A suspension of finely divided N-(2-fluoro phenyl) maleamic acid (14.2 g, 0.068 moles) in a solution of anhydrous sodium acetate (3.46 g)(Panreac, S.A.) in anhydrous acetic acid (95.0 %) (34.67 g, 0.340 moles)(Probus, S.A.) was stirred vigorously at 90 °C in a 250 ml round-bottomed three-necked flask. The flask was fitted with a condenser, mechanical stirrer and a thermometer. Heating and stirring were maintained for 1 hr. The mixture was stirred for two hours at room temperature to complete the formation of a bright yellow crystalline mass. The cooled reaction mixture was then poured slowly into a vigorously stirred slurry of ice and water (500 ml) for 1 hr. The yellow crystals were collected by filtration, washed repeatedly with cold distilled water, and dried under reduced pressure at 40 °C to give 10.25 g of crude N-(2-fluoro phenyl) maleimide (79.0 %). Recrystallization from a mixture of ethanol-water (1:2) converted this product to a prismatic quadrangular crystals melting at 76 °C. Analysis. Found: C, 62.64; H, 3.18; N, 7.32. $C_{10}H_6O_2NF$ requires C, 62.82; H, 3.14; N, 7.32. IR(KBr), the structure O=C-N-C=O presents bands at 1775 cm^{-1} ν(C=O), 1715 cm^{-1} ν(C=O), 690 cm^{-1} δ(C=O), 1395 cm^{-1} ν(C-N-C) and 1150 cm^{-1}

ν(C-N-C); bands appearing at 865 cm^{-1} and 760 cm^{-1} are due to the 1.2-substitution in the aromatic ring. The ethylenic double bond band situated at 830 cm^{-1} is due to γ(C-H) in conjugation with C=O groups and other one at 3100 cm^{-1} ν(C-H). Band appearing at 1245 cm^{-1} is due to the C-F bond. NMR (CCl_4) present signals at 3.20 τ (ppm)(singlet, ethylenic) and at 2.75 τ (ppm)(multiplet, aromatic protons). Furthermore, the integration corresponds to the protons confirming the molecular structure. UV (ethanol) shows two maxima (λ = 262 nm; ε = 1400 and λ = 268 nm; ε = 1250), a minimum (λ = 247 nm; ε = 830) and a shoulder (λ = 256 nm; ε = 1120). TLC on silica gel and benzene-ethyl acetate (85:15) for elution showed one spot (R_f = 0.40).

N-(3-fluoro phenyl) maleimide

This material was prepared by a method similar to that used for (II). 15 g of N-(3-fluoro phenyl) maleamic acid (0.072 moles), was heated with 3.65 g of anhydrous sodium acetate and 73.1 g (0.72 moles) of acetic anhydride. On cooling 11.93 g (86.8 %) of the crude product separated. Recrystallization from ethanol-water (1:1) gave trapezoic plates crystal, m.p. 52.5 °C. Analysis. Found: C, 62.57; H, 3.07; N, 7.14. $C_{10}H_6O_2NF$ requires C, 62.82; H, 3.14; N, 7.32. IR (KBr), 3100 cm^{-1} ν(C-H), 1770 cm^{-1} ν(C=O), 1710 cm^{-1} ν(C=O), 1595 cm^{-1} ν(C=C), 1490 cm^{-1} ν(C=C), 1390 cm^{-1} ν(C-N-C), 1255 cm^{-1} ν(C-F), 1150 cm^{-1} ν(C-N-C), 835 cm^{-1} γ(C-H), 780 cm^{-1} (1.3-disubstitution), 695 cm^{-1} δ(C=O), 675 cm^{-1} (1.3-disubstitution). NMR (CCl_4), 3.20 τ (ppm)(ethylenic, singlet), 2.75 τ (ppm)(multiplet, aromatics). UV (ethanol), maxima (λ = 274 nm; ε = 7520 and λ = 280 nm; ε = 7070) and minimum (λ = 262 nm; ε = 7180). TLC, movil phase benzene-ethyl acetate (85:15)(R_f = 0.40).

N-(4-fluoro phenyl) maleimide

This compound was prepared by the procedure given for the above analog. 8 g of N-(4-fluoro phenyl) maleamic acid (0.038 moles) were heated with 1.94 g anhydrous sodium acetate and 38.96 g of acetic anhydride (0.38 moles). On cooling, 6.6 g (91.0 %) of the product separated as transparent needle crystals. Recrystallization from ethanol gave needles, m.p. 155 °C. Analysis. Found: C, 62.94; H, 3.12; N, 7.52. $C_{10}H_6O_2NF$ requires C,. 62.82; H, 3.14; N, 7.32. IR (KBr), 3100 cm^{-1} ν(C-H), 1770 cm^{-1} ν(C=O), 1710 cm^{-1} ν(C=O), 1600 cm^{-1} ν(C=C), 1515 cm^{-1} ν(C=C), 1395 cm^{-1} ν(C-N-C), 1230 cm^{-1} ν(C-F), 1155 cm^{-1} ν(C-N-C), 835 cm^{-1} γ(CH), 825 cm^{-1} (1.4-disubstitution), 690 cm^{-1} δ(C=O). NMR, 3.20 τ (ppm)(ethylenics, singlet), 2.70 τ (ppm)(aromatic, multiplet). UV (dioxane), maximum (λ = 310 nm; ε = 380), minimum (λ = 287 nm; ε = 330) and a shoulder (λ = 264 nm; ε = 970). TLC, benzene-ethyl acetate (85:15), (R_f = 0.40).

N-(2.4-difluoro phenyl) maleimide

This compound was prepared by the procedure given for the above analog. 15 g of N-(2.4-difluoro phenyl) maleamic acid (0.066 moles), 3.36 g of anhydrous sodium acetate and 67.32 g (0.66 moles) of acetic anhydride gave 13.05 g (94.5 %) of crude N-(2.4-difluoro phenyl) maleimide. Recrystallization from ethanol-water (1:2) gave white needles, m.p. 84.0 °C. Analysis. Found: C, 57.25; H, 2.41; N, 6.67. $C_{10}H_5O_2NF_2$ requires C, 57.41; H, 2.39; N, 6.69. IR (KBr), 3100 cm^{-1} ν(C-H), 1775 cm^{-1} ν(C=O), 1715 cm^{-1} ν(C=O), 1600 cm^{-1} ν(C=C), 1515 cm^{-1} ν(C=C), 1395 cm^{-1} ν(C-N-C), 1275 cm^{-1} ν(C-F), 1145 cm^{-1} ν(C-N-C), 865 cm^{-1} (1.2.4-trisubstitution), 830 cm^{-1} γ(C-H), 690 cm^{-1} δ(C=O). NMR, 3.20 τ (ppm)(ethylenic, singlet), 2.95 τ (ppm)(aromatic, multiplet). UV (ethanol), maxima (λ = 262 nm;

ϵ = 1590 and λ = 266 nm; ϵ = 1560), minimum (λ = 247 nm; ϵ = 1100) and a shoulder (λ = 294 nm; ϵ = 810). TLC, benzene-ethyl acetate (85:15) (R_f = 0.44).

N-(2.5-difluoro phenyl) maleimide

In a similar reaction to the above analogs, a mixture of 13.0 g of N-(2.5-difluoro phenyl) maleamic acid (0.057 moles), 2.92 g of anhydrous sodium acetate and 58.4 g (0.57 moles) of acetic anhydride (95 %) was heated. The resulting precipitate yields 10.2 g of N-(2.5-difluoro phenyl) maleimide (85.5 %). On recrystallization from ethanol-water (1:4) gave white leaflets, m.p. 97.0 °C. Analysis. Found: C, 57.26; H, 2.51; N, 6.80. $C_{10}H_5O_2NF_2$ requires C, 57.41; H, 2.39; N, 6.69. IR (KBr), 3090 cm^{-1} ν(C-H), 1780 cm^{-1} ν(C=O), 1710 cm^{-1} ν(C=O), 1510 cm^{-1} ν(C=C), 1380 cm^{-1} ν(C-N-C), 1220 cm^{-1} ν(C-F), 1165 cm^{-1} ν(C-N-C), 865 cm^{-1} (1.2.5-trisubstitution), 830 cm^{-1} γ(C-H), 820 cm^{-1} (1.2.5-trisubstitution), 690 cm^{-1} δ(C=O). NMR, 3.20 τ (ppm)(ethylenic, singlet), 2.85 τ (ppm) (aromatic, multiplet). UV (ethanol), maxima (λ = 269 nm; ϵ =3100 and λ = 274 nm; ϵ = 2910), minimum (λ = 246 nm; ϵ = 1180) and a shoulder (λ = 293 nm; ϵ = 1110). TLC, benzene-ethyl acetate (80:20)(R_f = 0.47).

N-(2.3.5.6-tetrafluoro phenyl) maleimide

By the procedure described above, 20.8 g (0.079 moles) of the N-(2.3.5.6-tetrafluoro phenyl) maleamic acid, 4.03 g of anhydrous sodium acetate and 80.7 g (0.79 moles) of acetic anhydride gave 17.04 g of crude N-(2.3.5.6-tetrafluoro phenyl) maleimide (88.0 %). The precipitate upon recrystallization from ethanol-water (1:1) gave colourless needles melting at 137 °C. Analysis. Found: C, 49.26; H, 1.34; N, 5.72. $C_{10}H_3O_2NF_4$ requires C, 48.97; H, 1.22; N, 5.71. IR (KBr), 3080 cm^{-1} ν(C-H), 1785 cm^{-1}

ν(C=O), 1725 cm^{-1} ν(C=O), 1510 cm^{-1} ν(C=C), 1365 cm^{-1} ν(C-N-C), 1265 cm^{-1} ν(C-F), 1145 cm^{-1} ν(C-N-C), 835 cm^{-1} γ(C-H), 695 cm^{-1} δ(C=O). NMR, 3.00 τ (ppm)(ethylenic, singlet), 2.70 τ (ppm)(aromatic, multiplet). UV (ethanol), maximum (λ = 267 nm; ε = 2560), minimum (λ = 248 nm; ε =1620) and a shloulder (λ = 293 nm; ε = 350). TLC, for elution benzene-ethyl acetate (80:20) (R_f = 0.49).

N-(pentafluoro phenyl) maleimide

In a similar reaction, N-(pentafluoro phenyl) maleamic acid, 18.9 g (0.067 moles), anhydrous sodium acetate, 3.43 g and acetic anhydride 68.7 g (0.67 moles) reacted to give the corresponding N-(pentafluoro phenyl) maleimide. This was isolated giving 16.7 g of crude product (94.3 %). This product upon crystallization from n-hexane gives thin needles, melting at 105.5 °C. Analysis. Found: C, 45.43; H, 0.78; N, 5.23. $C_{10}H_2O_2NF_5$ requires C, 45.62; H, 0.76; N, 5.32. IR (KBr), 3095 cm^{-1} ν(C-H), 1780 cm^{-1} ν(C=O), 1730 cm ν(C=O), 1520 cm^{-1} ν(C=C), 1360 cm^{-1} ν(C-N-C), 1295 cm^{-1} ν(C-F), 1145 cm^{-1} ν(C-N-C), 825 cm^{-1} γ(C-H), 695 cm^{-1} δ(C=O). NMR, 3.00 τ (ppm)(ethylenic, singlet). UV (ethanol), shoulder (λ = 260 nm; ε =3730). TLC, for elution benzene-ethyl acetate (80:20)(R_f = 0.48).

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REFERENCES

1 J. González Ramos, J.M. Barrales-Rienda and M. Sánchez Chaves, Anales Quím. (Madrid),

2 J.M. Barrales-Rienda, J. González Ramos and M.Sanchez Chaves, J. Polym. Sci.

3 L.E. Coleman, Jr., J.F. Bork and H. Dunn, Jr., J. Org. Chem., 24 (1959) 135.

4 L.H. Flett and W.H. Gardner, Maleic Anhydride Derivatives, John Wiley, New York, 1952, p. 106.

5 R. Anschütz and Q. Wirtz, Ann., 239 (1887) 137. R. Anschütz, Ber., 20 (1887) 3214.

6 D.H. Marrian, J. Chem. Soc., (1949) 1515.

7 R. Lukeš and M. Pergál, Coll. Czech. Chem. Comm., 27 (1962) 1387.

8 N.E. Searle, U.S. Patent, 2.444.536, July 6, 1948. C.A. 42 (1948) 7340; H.W. Arnold and N.E. Searle, U.S. Patent, 2.462.835, C.A. 43 (1949) 4421.

9 L.F. Orlova, V.S. Ivanov and I. V. Vasil'eva, Vest. Leningrad. Univ. Fiz. Khim., 10 (1972) 131.

10 J.J. Giammaria, U.S. Patent, 2.669.555 (1950); J.J. Giammaria, U.S. Patent, 2.727.862 December, 20 (1955).

11 P. Kovacic and R.W. Hein, J. Am. Chem. Soc., 81 (1959) 1187; P. Kovacic and R.W. Hein, J. Am. Chem. Soc., 81 (1959) 1190.

12 P. Kovacic, U.S. Patent, 2.818.405 (1957), C.A. 52 (1958) 5018.

13 M.K. Hargreaves, J.G. Pritchard and H.R. Dave, Chem. Rev. 70 (1970) 439.

14 T. Uno and K. Machida, Bull. Chem. Soc. Japan, 35 (1962) 276; P. Chiorboli and P. Mirone, Ann. Chim. (Rome), 42 (1952) 681; P. Mirone, Ann. Chim. (Rome), 46 (1956) 39; T. Matsuo, Bull. Chem. Soc. Japan, 37 (1964) 1844; P. Bassignana, C. Cogrossi, G. Polla-Mattiot and M. Gillio-Tos, Spectrochim. Acta, 18 (1962) 809; R.J. Cotter, C.K. Sauers and J.M. Whelan, J. Org. Chem., 26 (1961) 10.

15 T. Matsuo, Can. J. Chem., 45 (1967) 1829; D. Bryce-Smith and M.A. Hems, J. Chem. Soc. (B) (1968) 812; T. Matsuo, J. Chem. Soc. Japan, Ind. Chem. Sect., 68 (1965) 1422. J. Ronayne and D.H. Williams, J. Chem. Soc. (B), (1967) 805; V. Gómez and R. Parellada, Anales Quím. (Madrid), 72 (1976) 401.