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Condensation of Nitro- and Amino-Substituted Phenylmaleimides with Furfuryl Alcohol

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Abstract—Reaction of nitro- and amino-substituted phenylmaleimides with furfuryl alcohol afforded 4-aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-[nitro(amino)phenyl]tricyclo[5.2.$1^{1.7}$.$0^{2.6}$]dec-8-enes. The latter were easily converted into the corresponding phosphites under the action of hexaethyltriamidophosphite.

Keywords: *N*-nitro(amino)phenylmaleimides, furfuryl alcohol, diene synthesis, phosphorylation

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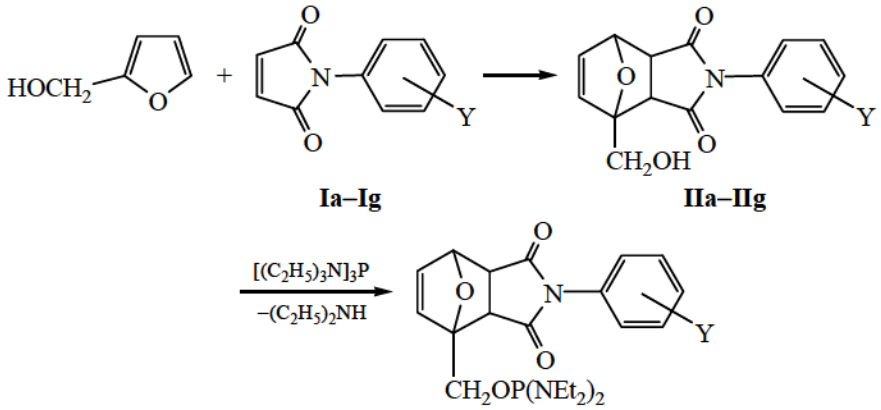
Reactions of [4+2] cycloaddition of maleimides to different conjugated dienes are widely used in the synthesis of fused heterocyclic compounds [1]. In particular, the use of functional furan derivatives in diene synthesis [2, 3] is of increasing interest which is due the possibility of obtaining adducts with potentially high biological activity. In this connection we studied the reaction of nitro- and amino-substituted phenylmaleimides **Ia**–**Ig** with furfuryl alcohol.

We found that interaction of imides **Ia**–**Ig** with furfuryl alcohol afforded 4-aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-[nitro(amino)phenyl]tricyclo[5.2.$1^{1.7}$.$0^{2.6}$]-dec-8-enes **IIa**–**IIg**. The latter can be easily converted into bis(*N*,*N*-diethylamido)(4-aza-4-aryl-10-oxa-3,5-dioxotricyclo[5.2.$1^{1.7}$.$0^{2.6}$]dec-8-en-1-yl)methylphosphites **IIIa**–**IIIg** by the action of an equimolar amount of hexaethyltriamidophosphite in anhydrous benzene or 1,4-dioxane under nitrogen atmosphere (Scheme 1).

The structure of the compounds obtained was confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy methods.

Scheme 1.



Ia–Ig **IIa–IIg**

IIIa–IIIg

Y = 2-NO_2 (**a**), 3-NO_2 (**b**), 4-NO_2 (**c**), 4-NHC(O)CH_3 (**d**), 3-NHC(O)Ph (**e**), 2-NC_5H_{10} (**f**), 4-$C_6H_5N_2$ (**g**).

EXPERIMENTAL

IR spectra were recorded on a FSM-1202 IR Fourier spectrometer in the range of 400–4000 cm^{-1} from mulls in mineral oil. ^1H and ^{13}C NMR spectra were registered on a JEOL JNM-ECX400A spectrometer, internal reference TMS. Purity of the obtained compounds was monitored by TLC on Silufol plates, eluting with a mixture ethanol–benzene (4 : 1) and detecting with iodine vapors.

4-Aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-(*o*-nitrophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-ene (IIa). To a solution of 0.59 g (0.0025 mol) of *N*-(*o*-nitrophenyl)maleimide in 8 mL of anhydrous benzene at 20°C was added 0.25 g (0.0025 mol) of furfuryl alcohol. The mixture was kept at 20°C for 48 h. The formed precipitate was filtered off and dried at room temperature. Yield 0.52 g (61%), mp 149–150°C. IR spectrum, ν, cm^{-1}: 3531 s (O–H), 3080, 3059 w (H–C=), 1774 m (C=O_s), 1703 s (C=O_{as}), 1606 m (C=C), 1578, 1485 m (C–C_{Ar}), 1523 s (N–O_{as}), 1355 s (N–O_s), 1313 m (C–N–C_s), 1189 s (C–N–C_{as}), 1064, 1032 m (C–O), 788, 724 m [δ(C–H)]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.03 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.22 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.79 m and 4.06 m (2H, CH_2O), 4.91 br.s (1H, OH), 5.20 s (1H, C^7H), 6.57 s (2H, CH=CH), 7.32–8.12 m (4H, C_6H_4). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 49.16 (C^6), 51.58 (C^2), 59.32 (CH_2OH), 80.93 (C^1), 92.73 (C^7), 134.71, 135.47, 137.30, 138.81, 139.11, 145.82 (C_6H_4), 125.53, 130.73 (CH=CH), 173.85, 175.30 (C=O). Found, %: C 66.51; H 3.80; N 8.98. $C_{15}H_{12}N_2O_6$. Calculated, %: C 66.46; H 3.79; N 8.86.

Compounds **IIb–IIg** were prepared similarly.

4-Aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-(*m*-nitrophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-ene (IIb). Yield 61%, mp 205–207°C. IR spectrum, ν, cm^{-1}: 3375 br.s (O–H), 3080 w (H–C=), 1720 s (C=O), 1600 m (C=C), 1510, 1488 m (C–C_{Ar}), 1532 s (N–O_{as}), 1351 s (N–O_s), 1259 m (C–N–C_s), 1191 m (C–N–C_{as}), 1073, 1010 m (C–O), 886, 809, 741 m [δ(C–H)]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.02 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.21 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.77 m and 4.05 m (2H, CH_2O), 4.93 br.s (1H, OH), 5.21 s (1H, C^7H), 6.56 s (2H, CH=CH), 7.15–8.23 m (4H, C_6H_4). Found, %: C 66.47; H 3.79; N 9.02. $C_{15}H_{12}N_2O_6$. Calculated, %: C 66.46; H 3.79; N 8.86.

4-Aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-(*p*-nitrophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-ene (IIc). Yield 64%, mp 190–191°C. IR spectrum, ν, cm^{-1}: 3382 s (O–H), 3081, 3040 w (H–C=), 1707 s (C=O), 1598 m (C=C), 1512, 1499 m (C–C_{Ar}), 1562 s (N–O_{as}), 1334 s (N–O_s), 1306 m (C–N–C_s), 1228 s (C–N–C_{as}), 1040 m (C–O), 857, 750 m [δ(C–H)]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.04 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.20 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.78 m and 4.07 m (2H, CH_2O), 4.92 br.s (1H, OH), 5.20 s (1H, C^7H), 6.58 s (2H, CH=CH), 7.73 d and 8.16 d (4H, C_6H_4, $^3J_{HH}$ 7.86 Hz). Found, %: C 66.49, H 3.81, N 9.00. $C_{15}H_{12}N_2O_6$. Calculated, %: C 66.46, H 3.79, N 8.86.

4-Aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-(*p*-acetylaminophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-ene (IId). Yield 72%, mp 206–207°C. IR spectrum, ν, cm^{-1}: 3458 br. m (O–H), 3276 m (N–H), 3060 w (H–C=), 1706 s (C=O), 1661 s (NHC=O), 1605 m (C=C), 1539, 1513 m (C–C_{Ar}), 1314 m (C–N–C_s), 1189 s (C–N–C_{as}), 1019 s (C–O), 852, 824 m [δ(C–H)]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.01 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.19 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.80 m and 4.08 m (2H, CH_2O), 4.98 br.s (1H, OH), 5.22 s (1H, C^7H), 6.57 s (2H, CH=CH), 7.01–8.08 m (4H, C_6H_4), 9.01 s (NH). Found, %: C 62.07; H 4.77; N 8.46. $C_{17}H_{16}N_2O_5$. Calculated, %: C 62.19; H 4.82; N 8.53.

4-Aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-(*m*-benzoylaminophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-ene (IIe). Yield 80%, mp 96–98°C. IR spectrum, ν, cm^{-1}: 3468 br. m (O–H), 3381 m (N–H), 3063 w (H–C=), 1773 m (C=O_s), 1708 w (C=O_{as}), 1669 w (NHC=O), 1606 m (C=C), 1579 [δ(N–H)], 1533, 1495 m (C–C_{Ar}), 1302 m (C–N–C_s), 1189 s (C–N–C_{as}), 1070, 1033 m (C–O), 871, 844, 794 m (C–H). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 3.00 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.20 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.79 m and 4.09 m (2H, CH_2O), 4.97 br.s (1H, OH), 5.19 s (1H, C^7H), 6.56 s (2H, CH=CH), 7.11–8.51 m (9H, C_6H_5, C_6H_4), 9.93 s (1H, NH). Found, %: C 66.51; H 4.64; N 7.35. $C_{21}H_{18}N_2O_5$. Calculated, %: C 66.66; H 4.79; N 7.40.

4-Aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-(*o*-piperidin-1-yl-phenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-ene (IIf). Yield 71%, mp 77–79°C. IR spectrum, ν, cm^{-1}: 3467 br.s (O–H), 3072, 3033 w (H–C=), 1776 m (C=O_s), 1708 s (C=O_{as}), 1599 m (C=C), 1526, 1497 m (C–C_{Ar}), 1313 m (C–N–C_s), 1189 s (C–N–C_{as}), 1031 m (C–O), 758 m [δ(C–H)]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.55–1.63 m and 2.77–2.85 m (10H, $C_5H_{10}N$), 3.03 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.21 d (1H,

C^2H, $^3J_{HH}$ 6.12 Hz), 3.76 m and 4.05 m (2H, CH_2O), 4.94 br.s (1H, OH), 5.23 s (1H, C^7H), 6.57 s (2H, CH=CH), 6.69–7.01 m (4H, C_6H_4). Found, %: C 67.82; H 6.23; N 8.10. $C_{20}H_{22}N_2O_4$. Calculated, %: C 67.79; H 6.21; N 7.90.

4-Aza-1-hydroxymethyl-10-oxa-3,5-dioxo-4-*N*-(*p*-phenylazophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-ene (IIg). Yield 65%, mp 120–121°C. IR spectrum, ν, cm^{-1}: 3487 m (O–H), 3078, 3030 w (H–C=), 1778 m ($C=O_s$), 1705 s ($C=O_{as}$), 1598 m (C=C), 1538, 1499 m ($C–C_{Ar}$), 1299 m ($C–N–C_s$), 1172 s ($C–N–C_{as}$), 1044 m (C–O), 845 m [δ(C–H)]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.05 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.19 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.74 m and 4.04 m (2H, CH_2O), 4.97 br.s (1H, OH), 5.21 s (1H, C^7H), 6.56 s (2H, CH=CH), 7.51–8.02 m (4H, C_6H_4). Found, %: C 52.45; H 3.50; N 8.69. $C_{21}H_{17}N_3O_4$. Calculated, %: C 52.50; H 3.54; N 8.75.

Bis(*N*,*N*-diethylamido){4-aza-10-oxa-3,5-dioxo-4-*N*-(*o*-nitrophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-en-1-yl}methylphosphite (IIIa). To a solution of 0.316 g (0.001 mol) of compound **IIa** in 4 mL of anhydrous 1,4-dioxane at 20°C was added 0.247 g (0.001 mol) of hexaethyltriamidophosphite under inert atmosphere. The mixture was stirred at 40°C for 1 h, the white precipitate was filtered off and dried at room temperature. Yield 0.25 g (51%), mp 128–130°C, R_f 0.67. IR spectrum, ν, cm^{-1}: 3072 w (H–C=), 1717 s (C=O), 1607 m (C=C), 1578, 1492 m ($C–C_{Ar}$), 1531 s ($N–O_{as}$), 1329 s ($N–O_s$), 1060, 1021 s (C–O, P–O), 793, 721 m [δ(C–H)]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.06 t (12H, CH_3, $^3J_{HH}$ 7.10 Hz), 3.07 m (8H, CH_2N), 3.02 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.21 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.81 m and 4.05 m (2H, CH_2O), 5.19 s (1H, C^7H), 6.58 s (2H, CH=CH), 7.12–8.11 m (4H, C_6H_4). Found, %: C 56.53; H 6.45; N 11.49; P 6.42. $C_{23}H_{31}N_4O_6P$. Calculated, %: C 56.32; H 6.37; N 11.42; P 6.31.

Compounds **IIIb**–**IIIg** were prepared similarly.

Bis(*N*,*N*-diethylamido){4-aza-10-oxa-3,5-dioxo-4-*N*-(*m*-nitrophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-en-1-yl}methylphosphite (IIIb). Yield 91%, oil. IR spectrum, ν, cm^{-1}: 3072 w (H–C=), 1710 s (C=O), 1601 m (C=C), 1526 m ($C–C_{Ar}$), 1548 s ($N–O_{as}$), 1352 s ($N–O_s$), 1073, 1036 s (C–O, P–O), 893, 800, 736 m [δ(C–H)]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.05 t (12H, CH_3, $^3J_{HH}$ 7.10 Hz), 3.06 m (8H, CH_2N), 3.01 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.20 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.81 m and 4.01 m (2H, CH_2O), 5.22 s (1H, C^7H), 6.55 s (2H, CH=CH), 7.12–8.21 m (4H, C_6H_4). Found, %: C 56.21; H 6.28; N 11.32; P 6.19. $C_{23}H_{31}N_4O_6P$. Calculated, %: C 56.32; H 6.37; N 11.42; P 6.31.

Bis(*N*,*N*-diethylamido){4-aza-10-oxa-3,5-dioxo-4-*N*-(*p*-nitrophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-en-1-yl}methylphosphite (IIIc). Yield 99%, oil. IR spectrum, ν, cm^{-1}: 3085 w (H–C=), 1711 s (C=O), 1610 m (C=C), 1551, 1499 m ($C–C_{Ar}$), 1534 s ($N–O_{as}$), 1350 s ($N–O_s$), 1069, 1022 s (C–O, P–O), 855, 796 m [δ(C–H)]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.05 t (12H, CH_3, $^3J_{HH}$ 7.10 Hz), 3.07 m (8H, CH_2N), 3.03 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.21 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.81 m and 4.02 m (2H, CH_2O), 5.23 s (1H, C^7H), 6.57 s (2H, CH=CH), 7.71 d and 8.14 d (4H, C_6H_4, $^3J_{HH}$ 7.86 Hz). Found, %: C 56.42; H 6.26; N 11.31; P 6.22. $C_{23}H_{31}N_4O_6P$. Calculated, %: C 56.32; H 6.37; N 11.42; P 6.31.

Bis(*N*,*N*-diethylamido){4-aza-10-oxa-3,5-dioxo-4-*N*-(*p*-acetylaminophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-en-1-yl}methylphosphite (IIId). Yield 91%, oil. IR spectrum, ν, cm^{-1}: 3065 w (H–C=), 1707 s (C=O), 1662 s (NHC=O), 1610 m (C=C), 1542, 1515 m ($C–C_{Ar}$), 1064, 1022 s (P–O, C–O), 853, 820 m [δ(C–H)]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.05 t (12H, CH_3, $^3J_{HH}$ 7.10 Hz), 3.09 m (8H, CH_2N), 3.02 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.21 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.83 m and 4.04 m (2H, CH_2O), 5.22 s (1H, C^7H), 6.56 s (2H, CH=CH), 7.03–8.02 m (4H, C_6H_4), 9.02 s (1H, NH). Found, %: C 59.65; H 6.94; N 11.08; P 6.08. $C_{25}H_{35}N_4O_5P$. Calculated, %: C 59.75; H 7.02; N 11.15; P 6.16.

Bis(*N*,*N*-diethylamido){4-aza-10-oxa-3,5-dioxo-4-*N*-(*m*-benzoylaminophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]-dec-8-en-1-yl}methylphosphite (IIIe). Yield 93%, oil. IR spectrum, ν, cm^{-1}: 3263 m (N–H), 3060 w (H–C=), 1709 s (C=O), 1668 s (NHC=O), 1611 m (C=C), 1549, 1487 m ($C–C_{Ar}$), 1068, 1024 s (C–O, P–O), 791, 709 m [δ(C–H)]. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.04 t (12H, CH_3, $^3J_{HH}$ 7.10 Hz), 3.07 m (8H, CH_2N), 3.01 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.22 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.85 m and 4.05 m (2H, CH_2O), 5.18 s (1H, C^7H), 6.56 s (2H, CH=CH), 7.11–7.72 m (9H, C_6H_5, C_6H_4), 9.91 s (1H, NH). Found, %: C 63.71; H 6.56; N 9.81; P 5.43. $C_{30}H_{37}N_4O_5P$. Calculated, %: C 63.82; H 6.61; N 9.92; P 5.49.

Bis(*N*,*N*-diethylamido){4-aza-10-oxa-3,5-dioxo-4-*N*-(*o*-piperidin-1-yl-phenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]-dec-8-ene-1-yl}methylphosphite (IIIf). Yield 92%,

oil. IR spectrum, ν, cm^{-1}: 3060 w (H–C=), 1712 s (C=O), 1602 m (C=C), 1578, 1492 m (C–C_{Ar}), 1054, 1020 s (C–O, P–O), 730 m [δ(C–H)]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.05 t (12H, CH_3, $^3J_{HH}$ 7.10 Hz), 3.08 m (8H, CH_2N), 1.55–1.63 m and 2.77–2.85 m (10H, $C_5H_{10}N$), 3.01 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.23 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.81 m and 4.07 m (2H, CH_2O), 5.23 s (1H, C^7H), 6.56 s (2H, CH=CH), 6.61–7.01 m (4H, C_6H_4). Found, %: C 63.56; H 7.79; N 10.71; P 5.77. $C_{28}H_{41}N_4O_4P$. Calculated, %: C 63.62; H 7.82; N 10.60; P 5.86.

Bis(*N*,*N*-diethylamido){4-aza-10-oxa-3,5-dioxo-4-*N*-(*p*-phenylazophenyl)tricyclo[5.2.1$^{1.7}$.0$^{2.6}$]dec-8-en-1-yl}methylphosphite (IIIg). Yield 95%, oil. IR spectrum, ν, cm^{-1}: 3075, 3032 w (H–C=), 1709 s (C=O), 1600 m (C=C), 1532, 1493 m (C–C_{Ar}), 1069, 1042 s (P–O, C–O), 842 m [δ(C–H)]. ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.05 t (12H, CH_3, $^3J_{HH}$ 7.10 Hz), 3.08 m (8H, CH_2N), 3.04 d (1H, C^6H, $^3J_{HH}$ 6.12 Hz), 3.18 d (1H, C^2H, $^3J_{HH}$ 6.12 Hz), 3.71 m and 4.02 m (2H, CH_2O), 5.20 s (1H, C^7H), 6.55 s (2H, CH=CH), 7.52–8.01 m (4H, C_6H_4). Found, %: C 63.22; H 6.51; N 12.67; P 5.60. $C_{29}H_{36}N_5O_4P$. Calculated, %: C 63.37; H 6.60; N 12.74; P 5.64.

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