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Synthesis of some novel 4-aza-tricyclo[5.2.2.0^{2,6}]undecane-3,5,8-triones from 2-trimethylsilyloxy-1,3-cyclohexadiene and 1-methoxy-1,3-cyclohexadiene

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Abstract: The synthesis and characterization of nine novel Diels-Alder cycloadducts: the 4-aza-tricyclo[5.2.2.0^{2,6}] undecane-3,5,8-triones using 2-trimethylsilyloxy-1,3-cyclohexadiene and 1-methoxy-1,3-cyclohexadiene is reported. The isolated yields of the pure cycloadducts range between 75 to 95%.

Keywords: Diels-Alder reaction; 1,3-cyclohexadienes; maleimides; cycloadducts; 4-aza-tricyclo[5.2.2.0^{2,6}] undecane-3,5,8-triones.

1. Introduction

The Diels-Alder [$_{\pi}4_s+_{\pi}2_s$] cycloaddition reaction is the most important reaction for the construction of six-membered cyclic compounds. The reaction constructs the six-membered ring in a regio- and stereo-controlled manner. A wide variety of dienes, dienophiles and catalyst combinations have been identified for this reaction, owing to the interesting class of stereospecific *endo*-isomer predominating in the resulting Diels-Alder cycloadducts.[1-6] Allylsilanes, vinylsilanes and silylenolethers are some of the reagents which have been used for the construction of the cyclic compounds in organic synthesis.[7-9] The methoxy- and trimethylsilyloxy-substituted 1,3-cyclohexadienes[10-11] especially have been widely used to prepare many interesting compounds including natural products and pharmacological compounds,[12-13] showing antituberculous, anticancer, psychotherapeutic and other biological activity.[14] Recently 3,8-diazabicyclo[3.2.1]octane analogues and 4-azatricyclo[5.2.2.0$^{2.6}$]undecane-3,5,8-triones derivatives have been investigated as potential agents for the inhibitory effects of antiproliferation and HIV-1 multiplication in MT-4 cells respectively.[15]

Our laboratory is primarily involved in the synthesis, characterization and reactions of some novel cyclic vinylsilanes, silylenolethers and other organosilyl- based compounds.[16-20] In this article, we wish to report synthesis and characterization of nine novel [$_{\pi}4_s+_{\pi}2_s$] cycloadducts from 2-trimethylsilyloxy-1,3-cyclohexadiene (**3a**) and 1-methoxy-1,3-cyclohexadiene (**3b**) using three different substituted maleimides.

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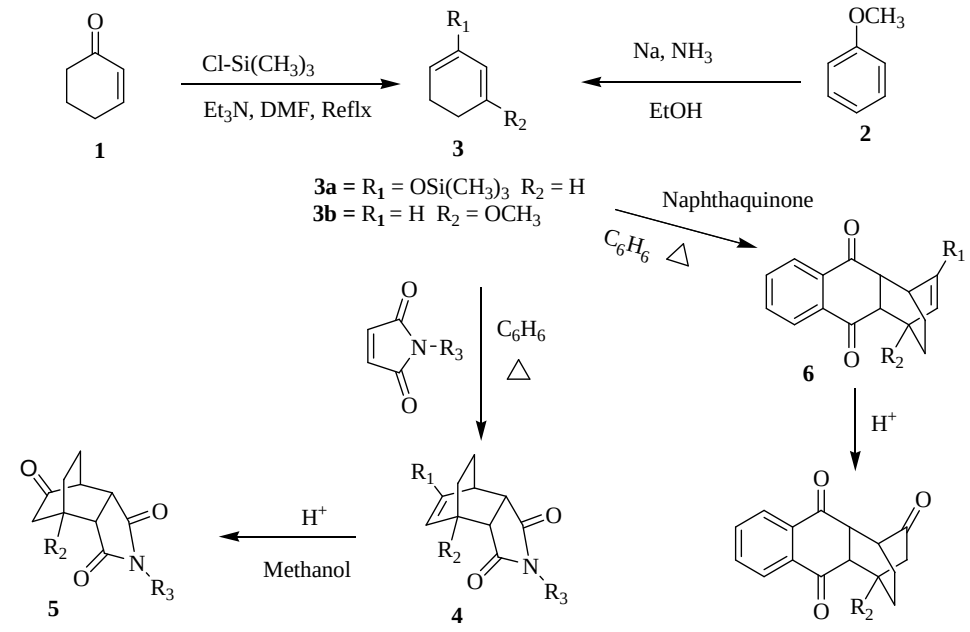
2. Results and Discussion

Cyclohexenone (**1**) was converted to 2-trimethylsilyloxy-1,3-cyclohexadiene (**3a**) by reaction with chlorotrimethylsilane in dry dimethylformamide and triethylamine.[21-22] Anisole (**2**) was subjected to Birch reduction to obtain 1-methoxy-1,3-cyclohexadiene (**3b**).[23-24] The compounds **3a** or **3b** upon reaction with three substituted maleimides: N-benzylmaleimide, N-ethylmaleimide and N-(4-acetylphenyl)maleimide in 1:2 ratio, in refluxing benzene solvent gave the Diels-Alder cycloadducts **4a**–**4f**. Progress of the reaction was followed by GC until complete conversion of the starting dienophile. GC analysis indicated compounds **4a** and **4b** to have formed in 95% yield, along with 5% stable hydrolyzed ketones **5a** and **5b**.[25] In case of **4c**, 81% of silylated product was found to have formed. Reaction of 1-methoxy-1,3-cyclohexadiene with the three maleimides gave the Diels-Alder cycloadducts **4d**-**4f**.

Further hydrolysis of compounds **4a** and **4b** by treatment with 2% hydrochloric acid in methanol gave only **5a** and **5b** respectively in 30 minutes. In our experiments, we have found that among all the maleimides, N-benzylmaleimide to be more reactive than the other maleimides with excellent yields of compounds **4b** and **4e** in short duration of time. The reactions are illustrated in Scheme 1.



5a, R_2 = H R_3 = Ethyl

5b, R_2 = H R_3 = Benzyl

4a, R_1 = $OSi(CH_3)_3$ R_2 = H R_3 = Ethyl

4b, R_1 = $OSi(CH_3)_3$ R_2 = H R_3 = Benzyl

4c, R_1 = $OSi(CH_3)_3$ R_2 = H R_3 = Ph-4-CO-CH_3

4d, R_1 = H R_2 = OCH_3 R_3 = Ethyl

4e, R_1 = H R_2 = OCH_3 R_3 = Benzyl

4f, R_1 = H R_2 = OCH_3 R_3 = Ph-4-CO-CH_3

6, R_1 = $OSi(CH_3)3$ R_2 = H

7, R_2 = H

Scheme-1. Synthesis of novel 4-aza-tricyclo[5.2.2.$0^{2,6}$]undecane-3,5,8-triones and 3-trimethylsilyloxy-1,4,4a,9a-tetrahydro-1,4-ethano-anthraquinones.

Similar Diels-Alder cycloaddition of **3a** with naphthalene-1,4-dione in refluxing benzene for 72 h gave 3-trimethylsilyloxy-1,4,4a,9a-tetrahydro-1,4-ethano-anthraquinone (**6**) in 80% yield. Mild acid hydrolysis with hydrochloric acid gave tetrahydro-1*H*-1,4-ethano-anthracene-2,9,10-trione as a yellow coloured solid (**7**). For the first time we are reporting the novel compounds of the silylenol ethers of anthraquinone derivatives **6**. These anthraquinone derivatives which are electron deficient, are proved to be promising molecules of biological importance and in material science chemistry.[26]

The yields and time required for the formation of products **4a-f**, **5a** and **5b**, **6** and **7** and their physical constants are indicated in Table 1.

Table 1. Physicochemical data for the compounds **4a-4f**, **5a**, **5b**, **6** and **7**

Compounds	Time (hrs)	Yields (%)	Mp(^{o}C)
4a	24	95	80-82
4b	12	97	113-115
4c	48	81	271-273
4d	24	80	112-114
4e	12	90	127-129
4f	48	95	153-155
5a	30 min	87	88-90
5b	30 min	90	125-127
6	72	74	114-116
7	01	80	192-194

In all the reactions, we expect the products to have formed to have exclusively the *endo*-configuration, in conformity with the reactions reported in literature.[1]

3. Conclusion

We report the synthesis and characterization of nine novel 3-trimethylsilyloxy-1,4,4a,9a-tetrahydro-1,4-ethano-anthraquinone as a new class of silyl enol ether, 4-aza-tricyclo[5.2.2.$0^{2,6}$]undecane triones, and their stable hydrolyzed compounds of aza-tricyclo[5.2.2.$0^{2,6}$]undec-8-ene-3,5-dione, and tetrahydro-1H-1,4-ethano-anthracene-2,9,10-trione.

4. Experimental

4.1 Materials and Characterization

All maleimides and solvents were commercial. IR spectra were recorded on Shimadzu FTIR-8400 spectrophotometer. All synthesized adducts were soluble in varying proportion of organic solvents like Acetone, dichloromethane, diethyl ether, chloroform and Ethyl acetate. All melting points remain uncorrected. Melting points were determined using polarizing optical microscopy using Olympus BX50 microscope equipped with a heating hot stage Mettler FP82HT and a central processor Mettler FP80. ^{1}H-NMR 400 MHz) and ^{13}C-NMR (100 MHz) spectra were recorded in $CDCl_3$ with a Bruker AMX 400 spectrometer using tetramethylsilane as an internal standard. GC-MS was carried out using Shimadzu QP 5050A instrument equipped with a 30 m length and 0.32 mm diameter BP-5 capillary column. Elemental analysis was carried out using Carlo-Erba 1106 analyser.

4.2 General procedure for the preparation of cycloadducts

All reactions were carried out on 0.500g scales. A mixture of 2-trimethylsilyloxy 1,3-cyclohexadiene (0.500g, 1.0 molar equivalent) and 1-substituted-1*H*-pyrrole-2,5-dione (0.184g 0.5 molar equivalent) was stirred at reflux temperature in dry benzene for two days. Progress of the reaction was monitored by GC-MS. After complete disappearance of the dienophile, the reaction mixture was cooled and washed with 5% potassium bicarbonate solution, water and concentrated under reduced pressure. The crude mass was extracted in to ethyl acetate, and dried with an, $MgSO_4$. Concentration and removal of solvent left a crude solid, which was recrystallized with 2:8 ratio ethyl acetate in hexane to obtain a white solid. Similar reactions with the dienophiles afforded **4d-4f.**

4-Ethyl-8-trimethylsilyloxy-4-aza-tricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (4a) : IR (KBr): ν = 2955, 2872 (alkyl -CH_2-), 1770 (C=O), 1444 (Ar-CH=CH-), 1402 (-CH=CH-), 1253 (-Si$(CH_3)_3$ cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 4.87 (d, 1H, *J* = 2.1), 3.56-3.45 (qr, 2H, *J* = 6.8 Hz), 3.12-2.74 (m, 4H), 2.27-1.79 (m, 4H), 1.11 (t, 3H, *J* = 6.8), 0.17 (s, 9H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 177.6, 176.6, 154.3, 115.2, 43.8, 42.6, 42.5, 33.7, 32.5, 31.2, 25.2, 12.5, 0.2 ppm; GC-MS *m/z*: 293 (5.15), 278 (1.73), 265 (6.59), 237 (2.56), 193 (5.25), 168 (53.79), 166 (14.47), 151 (23.64), 127 (21.63), 110 (1.91), 91 (12.93), 73 (100), 55 (15.82), 45 (18.46); Anal. Calcd for $C_{15}H_{23}NO_3Si$: C, 61.40%; H 7.90%, N 4.77%. Found: C, 61.71%; H 7.85%, N 4.68%.

4-Benzyl-8-trimethylsilyloxy-4-aza-tricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (4b) : IR: 2955, 2856 (alkyl -CH_2), 1770 (C=O), 1633 (Ar-CH=CH-), 1402 (-CH=CH-), 1251(-OSi-$CH_3)_3$ cm^{-1}; ^{1}H-NMR δ = 7.32 (m, 5H), 4.86 (m, 1H), 4.84 (s, 2H), 3.13-2.74 (m, 4H), 1.58 (m, 4H), 0.12 (s, 9H) ppm; ^{13}C-NMR δ = 178.6, 177.8, 154.3, 135.9, 128.5, 128.4, 127.6, 101.3, 45.1, 44.5, 42.1, 37.6, 32.2, 25.2, 24.1, 0.02 ppm; GC-MS *m/z*: 355 (4.88), 327 (2.51), 193 (6.16), 189 (11.90), 169 (6.24), 168 (46.62), 166 (11.61), 153 (4.72), 151 (18.53), 132 (2.55), 121 (1.23),104 (5.45), 91 (100), 77 (12.59), 75 (14.60), 73 (94.89), 65 (16.59), 45 (13.64); Anal. Calcd for $C_{20}H_{25}NO_3Si$: C, 67.57%; H, 7.09%; N 3.94%. Found: C, 67.74%; H 6.80%; N, 3.57%.

4-(4-Acetyl-phenyl)-8-trimethylsilyloxy-4-aza-tricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (4c) : IR: 2924, 2854, (alkyl -CH_2-), 1708 (C=O), 1460 (Ar-CH=CH-), 1298 (-CH=CH-), 1267(-OSi-$CH_3)_3$ cm^{-1}; ^{1}H-NMR δ = 8.05 (d, 2H, *J* = 8.8), 7.37 (d, 2H, *J* = 8.8), 5.01 (d, 1H, *J* = 2.4), 3.33-2.86 (m, 4H), 2.61 (s, 3H), 2.34-1.86 (m, 4H), 0.24 (s, 9H) ppm; ^{13}C-NMR δ = 210.3, 129.2, 126.4, 105.1, 42.9, 41.1, 38.1, 30.1, 26.7, 23.6, 21.8, 0.0 ppm; Anal. Calcd for $C_{21}H_{25}NO_4Si$: C, 65.77%; H 6.57%; N 3.65%. Found: C, 66.02%; H 6.80%; N 3.94%.

4-Ethyl-1-methoxy-4-aza-tricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (4d) : IR: 2906, 2854 (alkyl –CH_2-), 1693 (Ar-CH=CH-), 1226 (-CH=CH-) cm^{-1}; ^{1}H-NMR δ = 6.18 – 6.07 (m, 2H), 3.51(s, 3H), 3.45 (m, 2H), 3.13 (m, 2H), 2.92 (d, 1H, *J* = 2.3), 1.84-1.43 (m, 4H), 1.06 (m, 3H) ppm; ^{13}C-NMR δ = 177.9, 175.5, 134.4, 130.1, 78.3, 50.8, 45.2, 44.8, 33.4, 31.5, 27.1, 24.4, 12.9 ppm; GC-MS *m/z*: 236 (1.22), 208 (1.30), 207 (11.91), 164 (1.0), 150 (1.80), 135 (1.94), 127 (20.40), 121 (2.11), 111 (6.64), 110 (100), 108 (85.55), 95 (12.93), 80 (5.59), 77 (20.19), 65 (23.86), 56 (17.59), 41 (14.25); Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36%; H, 7.28%; N 5.95%. Found: C, 66.67%; H 7.56%; N 6.37%.

4-Benzyl-1-methoxy-4-aza-tricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (4e) : IR: 2945, 2872 (alkyl CH_2), 1770 (C=O), 1693 (C=O), 1496 (Ar-CH=CH-), 1290 (-CH=CH-) cm^{-1}; ^{1}H-NMR δ = 7.27 (m, 5H), 6.08-5.96 (m, 2H), 4.56 (s, 2H), 3.49 (s, 3H), 3.10-2.92 (m, 3H), 1.83-148 (m, 4H) ppm; ^{13}C-NMR δ = 177.7, 175.3, 135.8, 134.6, 130.2, 128.6, 128.4, 127.6, 78.3, 50.7, 45.3, 44.8, 42.1, 31.5, 27.0, 24.4 ppm; GC-MS *m/z*: 298 (2.50), 269 (2.60), 189 (7.68), 135 (4.23), 121 (1.66), 110 (100), 108 (58.61), 91 (28.56), 78 (20.37), 65 (20.11), 41 (11.33); Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71%; H, 6.44%; N, 4.71%. Found: C, 72.83%; H, 6.62%; N, 4.59%.

4-(4-Acetyl-phenyl)-1-methoxy-4-aza-tricyclo[5.2.2.0^{2,6}]undec-8-ene-3,5-dione (4f) : IR: 2926, 2852 (alkyl -CH_2-), 1712 (C=O), 1687 (C=O), 1600 (Ar-CH=CH-), 1269 (-CH=CH-) cm^{-1}; ^{1}H-NMR δ =

8.03-7.99 (m, 2H), 7.35 (m, 2H), 6.32-6.21 (m, 2H), 3.54 (s, 3H), 3.28-3.13 (m, 3H), 2.60 (s, 3H), 1.91-1.53 (m, 4H) ppm; ^{13}C-NMR δ = 134.8, 130.6, 128.9, 126.7, 50.9, 45.4, 45.1, 31.9, 29.7, 27.1, 26.6, 24.4, 0.0 ppm; Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14%; H, 5.89%; N, 4.31%. Found: C, 69.83%; H, 6.39%; N 4.0%.

4.3. General procedure for acid catalyzed hydrolysis products of stable ketones from silylated adducts

Compound **5a** (0.200 g) and 10 drops of dilute HCl in 5ml of methanol was stirred at room temperature for 30 minutes, extracted into dichloromethane, washed with dilute sodium bicarbonate solution and water, concentrated under reduced pressure. The crude product was re-crystallized with ethyl alcohol. The procedure was repeated for the synthesis of compound (**7).**

4-Ethyl-4-aza-tricyclo[5.2.2.$0^{2,6}$]undecane-3,5,8-trione (5a) : IR: 2941, 2872 (alkyl CH_2), 1714 (C=O), 1633 (-HC=CH-) cm^{-1}; ^{1}H-NMR δ = 3.55-3.51 (m, 2H), 3.14-3.00 (m, 2H), 2.74-2.40 (m, 4H), 1.89-1.53 (m, 4H), 1.19-1.15 (m, 3H) ppm; ^{13}C-NMR δ = 211.2, 179.1, 178.6, 47.6, 42.7, 41.7, 34.7, 33.4, 27.5, 23.3, 20.6, 12.8 ppm; GC-MS *m/z*: 221 (5.07), 193 (14.93), 153 (4.93), 95 (4.48), 81 (10.37), 80 (35.45), 79 (94.55), 77 (41.04), 76 (15.30), 69 (4.78), 56 (71.72), 42 (100); Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14%; H, 6.83%; N, 6.33%. Found: C, 65.35%; H, 6.79%; N, 6.40%.

4-Benzyl-4-aza-tricyclo[5.2.2.$0^{2,6}$]undecane-3,5,8-trione (5b) : IR: 2924, 2854 (alkyl CH_2), 1724 (C=O), 1697 (C=O), 1456 (Ar-CH=CH-), 1213 (-CH=CH-) cm^{-1}; ^{1}H-NMR δ = 7.31 (s, 5H), 4.66 (s, 2H), 3.12 (m, 1H), 3.0 (m, 1H), 2.97 (m, 1H), 2.72 (m, 1H), 2.15 (m, 2H), 2.09-1.75 (m, 4H) ppm; ^{13}C-NMR δ = 210.3, 177.5, 176.5, 135.4, 128.7, 128.1, 43.7, 42.6, 42.5, 40.7, 30.9, 29.9, 23.6, 22 ppm; GC-MS *m/z*: 283 (5.67), 132 (1.09), 106 (1.10), 104 (2.06), 96.4 (2.39), 95 (2.36), 93 (2.25), 92 (10.28), 91 (100), 79 (30.94), 77 (26.78), 65 (21.95), 53 (10.17), 51 (9.5), 42 (13.55); Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07%; H, 6.05%; N, 4.94%. Found: C, 71.80%; H, 5.78%; N 4.56%.

3-Trimethylsilyloxy-1,4,4a,9a-tetrahydro-1,4-ethano-anthraquinone (6) : IR: 2922, 2852 (alkyl CH_2), 1680 (C=O), 1631(Ar-CH=CH-), 1282 (-CH=CH-), 1234 $(-OSi-CH_3)_3$ cm^{-1}; ^{1}H-NMR δ = 8.14 (m, 2H), 7.80 (m, 2H), 4.95 (d, 1H, *J* = 2.5), 3.43-3.15 (m, 4H), 2.93-1.51 (m, 4H), 0.12 (s, 9H) ppm; ^{13}C-NMR δ = 198.6, 197.6, 155.9, 136.4, 136.1, 134.4, 134.3, 127.4, 127.1, 102.5, 51.6, 50.9, 42.1, 37.3, 26.5, 26.2, 0.0 ppm; Anal. Calcd for $C_{19}H_{22}O_3Si$: C, 69.90%; H, 6.79%. Found: C, 69.81%; H 6.74%.

3, 4, 4a, 9a-Tetrahydro-1H-1,4-ethano-anthracene-2,9,10-trione (7) : IR: 2924, 2854 (alkyl -CH_2-), 1730 (C=O), 1666 (Ar-CH=CH-), 1290 (-CH=CH-) cm^{-1}; ^{1}H-NMR δ = 8.13 (m, 2H), 7.74 (m, 2H), 4.15 (t, 1H, *J* = 2.6), 3.98 (m, 1H), 2.32-1.93 (m, 4H), 2.12-1.57 (m, 4H) ppm; ^{13}C-NMR δ = 208.7, 181.1, 180.9, 150.1, 143.5, 133.8, 132.3, 132.1, 126.6, 45.5, 38.9, 30.9, 29.7, 29.5, 24.1, 22.9 ppm; Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57%; H, 5.55%. Found: C, 76.05%; H, 5.05%.

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