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Synthesis and Diels–Alder Reactions of *N*-Methylthionomaleimide

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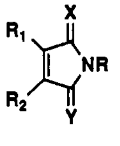
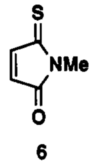
N-Methylthionomaleimide (**6**) has been synthesized. It is the first example of a thionomaleimide unsubstituted on the olefinic C atoms. Its dienophilic behavior at the olefinic center, with representative dienes (symmetrical and unsymmetrical), has been investigated. There is appreciable regioselectivity with terminally oxygenated unsymmetrical dienes, the O-substituted carbon of the diene adding preferentially to the thiono-substituted end of the olefin.

In contrast to the vast literature on maleimide and its derivatives, little is known about its thiocarbonyl analogs. The few known compounds of this type bear either one or two C substituents, as shown below (**1–5**). For none of them has any Diels–Alder reaction involving the ring double bond been reported, although reactions involving the thiocarbonyl function have been described.[1-3] We now report the synthesis of **6**, the first C-unsubstituted monothionomaleimide as well as a study of its dienophilic behavior with some representative dienes.





6

1 X = S; Y = O; R = R$_1$ = 4-tolyl; R$_2$ = H
2 X = S; Y = O; R = 4-tolyl; R$_1$ = cyclohexyl; R$_2$ = H
3 X = Y = S; R = 4-toluidino, R$_1$ = 4-tolyl; R$_2$ = H
4 X = Y = S; R = 4-tolyl; R$_1$ = cyclohexylamino; R$_2$ = H
5 X = S; Y = O; R = H; R$_1$ = Me; R$_2$ = Et

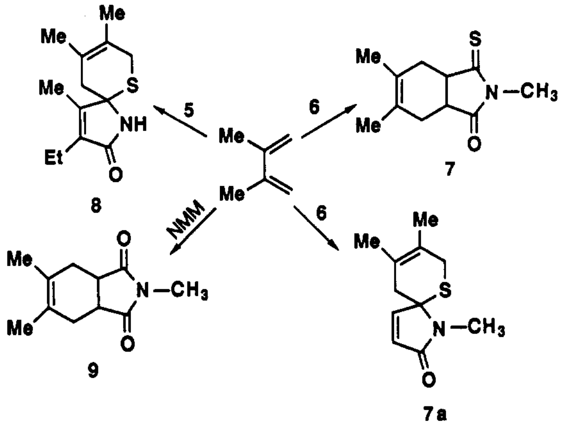
Results and Discussion

Direct thionation of the commercially available *N*-methylmaleimide (NMM) using Lawesson's reagent[4] under carefully defined conditions gave **6** in 44% yield. Thionomaleimide **6** is a highly crystalline purple, volatile compound which is stable over a period of several months in the refrigerator. At ambient temperature and in the presence of air and light it slowly turns yellow on the surface. Although its NMR spectrum shows this material to be still mainly **6**, NMM and oligomers of **6** are also present as indicated by MS. This is in marked contrast to the greater instability reported for the N-unsubstituted thiono imide **5**. In its UV-vis spectrum, **6** has maxima at 583, 544, 349, and 278 nm similar to those reported for **5**. Its NMR spectrum shows a doublet of doublets at δ 6.79 and 6.69, consistent with the structure, and its EI mass spectrum shows a strong molecular ion (100%) at 127.

Diels–Alder Reaction of 6 with a Symmetrical Diene (Table I). Thiono imide **6** reacts with 2,3-dimethylbutadiene in toluene at 70 °C for 5 h to give adduct **7** in 85% yield. At room temperature the same reaction requires 3 weeks to go to completion. No 4 + 2 adduct involving the thiocarbonyl moiety was detected. In contrast, the same diene is reported to add only to the thiocarbonyl function of **5** on standing in methylene chloride for 7 days to give the spiro adduct **8**.[1] In order to compare the dienophilic behavior of **6** and **5** under similar conditions, we carried out the reaction of **6** and 2,3-dimethylbutadiene in methylene chloride at room temperature. It was complete after 32 h, giving the olefinic and thione adducts **7** and **7a**, respectively, in a ratio of 90:10. Similar results were obtained when the reaction was carried out in other polar solvents, the ratio of **7**:**7a** in nitromethane and in chloroform being 93:7 and 95:5, respectively. A 5 M LiClO$_4$ ether solution has been reported to be a highly effective catalyst for Diels–Alder reactions.[5] When **6** and 2,3-dimethylbutadiene were reacted in 5 M ethereal LiClO$_4$ solution, the reaction was indeed greatly accelerated, the imide being consumed in 10 min. The product was a mixture of **7** and **7a** in which the spiro adduct predominated in a ratio of 44:56. Solvent polarity clearly influences the mode of cycloaddition, since polar solvents both speed up the reaction and increase the proportion of thiocarbonyl addition product. The spiro adduct **7a** is quite stable thermally and does not rearrange to **7** under conditions

Table I. Cycloaddition of 6 to 2,3-Dimethylbutadiene

solvents	temp, °C	reactn time	product ratio 7:7a	total yield (%)
toluene	70	5 h	100:0	87
toluene	rt	3 week	100:0	85
CH_2Cl_2	rt	32 h	90:10	85
$CHCl_3$	rt	32 h	93:7	81
CH_3NO_2	rt	32 h	95:5	88
$LiClO_4$/ether	rt	10 min	44:56	62



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(1) (a) Bishop, J. E.; Dagam, S. A.; Rapoport, H. *J. Org. Chem.* **1989**, *54*, 1876. (b) Bishop, J. E.; O'Connell, J. F.; Rapoport, H. *J. Org. Chem.* **1991**, *56*, 5079.

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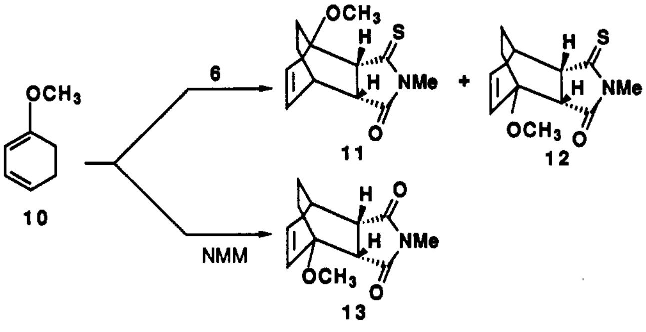
in which 7 is obtained as the sole product, i.e., in toluene at 70 °C or even at 120 °C, clearly indicating that it is not a labile kinetic product.

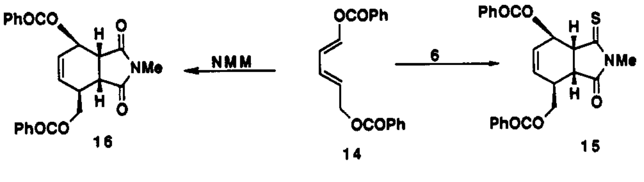
N-Methylmaleimide reacted with 2,3-dimethylbutadiene in toluene at 70 °C (5 h) to give adduct 9. A competitive reaction of NMM and 6 with 2,3-dimethylbutadiene under similar conditions gives adducts 9 and 7 in a ratio 100:81, indicating that 6 is slightly less reactive than NMM.

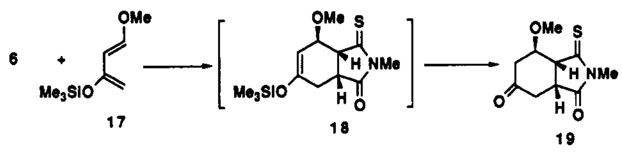
Diels–Alder Reaction of 6 with Unsymmetrical Dienes. Compound 6 exhibited a variable degree of regioselectivity in reactions with representative unsymmetrical dienes. In toluene solution at 70 °C, 6 reacted with 1-methoxy-1,3-cyclohexadiene (10)[6] to give a mixture of endo adducts 11 and 12 in the ratio of 2:1. The same products 11 and 12 were obtained in ethereal $LiClO_4$ in a ratio of 85:15. It is noteworthy that the predominant isomer in both reactions is that in which the methoxyl is adjacent to the thione function, and no thione addition product was detected. In comparison, the reaction of NMM with 10 in hot toluene afforded only endo adduct 13 in good yield (82%). In ethereal $LiClO_4$, the same reaction gave a poor yield (8%) of 13, no other product being isolated.



The reaction of thiono imide 6 with diene 14[7] afforded only adduct 15 in reasonable yield (58%). In comparison, NNM reacted with 14 to give the corresponding adduct 16 as the sole product (87%).

Excellent regioselectivity was also observed in the reaction of 6 with Danishefsky's diene. Ketone 19 was obtained as the only isolable product (56%), the initially produced adduct 18 being hydrolyzed on silica during chromatography.





In conclusion, the first C-unsubstituted monothionomaleimide has been prepared and was found to exhibit dienophilic behavior at the olefinic center as well as at the thiocarbonyl moiety. Polar solvents accelerated the cycloaddition and resulted in an increase of the spiro adduct derived from addition to the thiocarbonyl moiety. Good regioselectivity was observed with several terminally oxygenated unsymmetrical dienes, the O-substituted carbon of the diene adding preferentially to the thiono-substituted carbon of the dienophile.

Experimental Section

All melting points are uncorrected. All NMR spectra were recorded in $CDCl_3$, and chemical shifts are expressed in δ units. All FT-IR spectra were run as KBr plates. Elemental analyses were carried out by Atlantic Microlab, Atlanta, GA.

***N*-Methylthionomaleimide (6).** To a hot solution of NMM (1 g, 9 mmol) in dry toluene (30 mL) was added a boiling suspension of Lawesson's reagent (1.14 g, 5 mmol) in dry toluene (50 mL). The mixture was heated to boiling for 30 min. The cooled dark red solution was filtered quickly through silica under suction. The solvent was evaporated under reduced pressure. The residue was extracted with hexane. The extract was filtered and evaporated to give a red oil, which was purified by being passed through silica and eluted with benzene/cyclohexane (1:1), to give purple crystals (0.5 g), mp 44–45.5 °C, yield 44%. ^1H NMR: 6.79 (1 H, d, J = 5.78 Hz), 6.69 (1 H, d, J = 5.78 Hz), 3.30 (3 H, s) IR (cm^{-1}): 3143, 3103, 3088, 1727, 1710, 1701, 1696, 1437, 1345, 1288. UV–vis (hexane), λ_{max}: 209 nm (log ϵ, 4.27), 278 (3.92), 349 (3.65), 544 (0.91), 583 (0.79), 627 (0.38). MS: *m/e* 127 (M^+, 70), 113 (31). Anal. Calcd for C_5H_5NOS: C,47.23; H, 3.96. Found: C, 47.17; H, 3.93.

Adduct 7. A mixture of 6 (20 mg, 0.157 mmol) and 2,3-dimethylbutadiene (15.50 mg, 0.18 mmol) in toluene (4 mL) was heated at 70 °C for 5 h. The solvent was evaporated under reduced pressure, and the residue was purified by radial chromatography on silica with benzene–cyclohexane as eluent, to give 7 (28.76 mg) as a light yellow solid, mp 67–68 °C, yield 88%. ^1H NMR: 3.31 (1 H, ddd, J = 7.16 Hz, J = 8.40 Hz, J = 3.27 Hz), 3.23 (3 H, s), 3.00 (1 H, ddd, J = 7.03 Hz, J = 8.54 Hz, J = 3.25 Hz), 2.66 (1 H, dd, J = 14.85 Hz, J = 3.27 Hz), 2.40 (1 H, dd, J = 15.08 Hz, J = 2.95 Hz), 2.39 (1 H, ddd), 2.27 (1 H, ddd, J = 13.95 Hz, J = 4.18 Hz, J = 2.90 Hz), 1.63 (6 H, s). ^{13}C NMR: 216.37, 181.59, 127.28, 126.42, 77.35, 77.00, 76.64, 49.45, 40.33, 34.96, 30.88, 29.44, 19.77, 19.06. IR (cm^{-1}): 2982, 2945, 2909, 2849, 2843, 1742, 1695, 1448, 1431, 1380, 1329, 1308, 1261, 1198, 1012. MS: *m/e* 209 (M^+, 100), 194 (69), 176 (76), 166 (50), 148 (81), 127 (78). Anal. Calcd for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22. Found: C, 63.18; H, 7.21.

Adduct 7 in Toluene at Room Temperature. A solution of 6 (20 mg, 0.16 mmol) and 2,3-dimethylbutadiene (0.13 mL; 96 mg, 1.1 mmol) in toluene was stirred at room temperature. The reaction was complete in 3 weeks. The solvent was evaporated and radial chromatography of the residue on silica with hexane–benzene gave adduct 7 (27.9 mg, yield 85%).

Reaction in Ethereal Perchlorate Solution (7 and 7a). A mixture of 79 mg (0.62 mmol) of 6 [0.7 mL (0.45 g, 5.5 mmol) of 2,3-dimethylbutadiene] in 5 mL of 5 M $LiClO_4$ solution in ether was stirred at room temperature for 10 min. The reaction mixture was diluted with 20 mL of ether, washed with water (2 × 20 mL), and dried over magnesium sulfate. Evaporation of the solvent followed by radial chromatography on silica with hexane–chloroform gave 35 mg of 7 and 45 mg of 7a as a brown gum, total yield 62%. ^1H NMR of 7a: 7.13 (1 H, d, J = 5.75 Hz), 6.03 (1 H, d, J = 5.74 Hz), 3.36 (1 H, d, J = 16.17 Hz), 3.20 (1 H, d, J = 15.79 Hz), 3.18 (3 H, s), 2.67 (1 H, d, J = 15.63 Hz), 1.99 (1 H, d, J = 15.87 Hz), 1.78 (3 H, s), 1.70 (3 H, s). ^{13}C NMR: 169.62, 150.73, 125.88, 124.91, 123.76, 77.35, 77.00, 76.64, 71.04, 39.04, 32.06, 24.52, 20.22, 18.83. MS: *m/e* 209 (M^+, 73), 176 (100), 161 (97), 127 (70). HRMS: calcd for $C_{11}H_{15}NOS$ 209.0874. Found: 209.0878.

Diels–Alder Reaction in CH_2Cl_2 (7 and 7a). A solution of 6 (13.7 mg, 0.11 mmol) and 2,3-dimethylbutadiene (0.1 mL, 0.79 mmol) in methylene chloride (5 mL) was stirred at room temperature for 32 h. Standard workup gave a mixture of products 7 and 7a (20.0 mg) in a total yield of 88%, identified by NMR spectroscopy. HPLC analysis determined the ratio of 7:7a as 90:10.

Reaction in Chloroform. A solution of 6 (14.55 mg, 0.11 mmol) and 2,3-dimethylbutadiene (0.1 mL, 0.79 mmol) in chloroform (5 mL) was stirred for 32 h at room temperature. Standard workup gave a mixture of products 7 and 7a (19.0 mg) in a total

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yield of 81%. HPLC analysis determined the ratio of 7:7a as 95:5.

Reaction in Nitromethane. A mixture of 6 (12.53 mg, 0.10 mmol) and 2,3-dimethylbutadiene (0.1 mL, 0.79 mmol) in nitromethane (5 mL) was stirred for 32 h at room temperature. Standard workup gave a mixture of products 7 and 7a (17.5 mg), in a total yield of 81%, and HPLC analysis determined the ratio of 7:7a as 93:7.

Action of Heat on 7a. A solution of 7a (23 mg) in toluene (2 mL) was stirred at 70 °C for 5 h. The dark solution was evaporated and the ^{1}H NMR spectrum of the residue showed it to be 7a. Adduct 7a was also recovered unchanged after being refluxed in a toluene solution for 3 h.

Adduct 9. A solution of *N*-methylmaleimide (0.5 g, 4.5 mmol) and 2,3-dimethylbutadiene (0.85 mL; 0.55 g, 6.7 mmol) in toluene (10 mL) was heated at 70 °C for 5 h. The solvent was evaporated under reduced pressure and the residue was crystallized from hexane to give 9 as a white solid (0.8 g, yield 90%), mp 70–72 °C. ^{1}H NMR: 3.05 (2 H, t, *J* = 2.63 Hz), 2.97 (3 H, s), 2.45 (2 H, d, *J* = 14.66 Hz), 2.25 (2 H, d, *J* = 14.66 Hz). IR (cm^{-1}): 2992, 2949, 2913, 2897, 2861, 1771, 1764, 1694; 1684, 1471, 1444, 1433, 1383, 1325, 1284, 1018. MS: *m/e* 193 (M$^+$, 100), 178 (15), 166 (20), 112 (32), 108 (67), 107 (59). Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82. Found: C, 68.32; H, 7.81.

Competitive Reaction of 6 and NMM with 2,3-Dimethylbutadiene. To a solution of 6 (3.64 mg, 0.029 mmol) and NMM (3.37 mg, 0.031) in toluene (5 mL) was added 2,3-dimethylbutadiene (0.05 mL; 0.03 g, 0.3652 mmol). The mixture was stirred at 70 °C for 2 h, and the solvent was evaporated under reduced pressure. The residue was analyzed by HPLC, which showed that adducts 7 and 9 were present in the ratio of 81:100.)

Adducts 11 and 12. A solution of 6 (74 mg, 0.157 mmol) in toluene (10 mL) containing 1-methoxy-1,3-cyclohexadiene (0.33 mL, 1.8 mmol) was heated at 70 °C for 5 h. Evaporation of the solvent under reduced pressure followed by chromatography of the residue with hexane as eluent gave adduct 11 (59 mg), mp 94.5–95.5 °C, and adduct 12 (29 mg), mp 122–124 °C (total yield 63%).

Adduct 11. ^{1}H NMR: 6.07 (1 H, d, *J* = 8.70 Hz), 6.04 (1 H, dd, *J* = 8.25 Hz, *J* = 14.01 Hz), 3.52 (3 H, s), 3.47 (1 H, d, *J* = 7.87 Hz), 3.16 (3 H, s), 3.10 (1 H, m), 2.95 (1 H, dd, *J* = 3.12 Hz, *J* = 7.88 Hz), 1.94 (1 H, td, *J* = 9.45 Hz, *J* = 2.68 Hz), 1.73 (1 H, tt, *J* = 11.16 Hz, *J* = 3.03 Hz), 1.52 (1 H, tt, *J* = 11.89 Hz, *J* = 3.37 Hz), 1.44 (1 H, td, *J* = 11.85, *J* = 3.48 Hz). ^{13}C NMR: 209.35, 179.83, 134.94, 129.94, 79.05, 77.35, 77.00, 76.65, 52.95, 50.62, 46.38, 32.06, 28.79, 27.47, 24.43. IR (cm^{-1}): 3043, 2954, 1739, 1429, 1326, 1299, 1217, 1128, 1119. MS: *m/e* 237 (M$^+$, 46), 209 (24), 129 (62, 110 (100). Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37. Found: C, 60.82; H, 6.34.

Adduct 12. ^{1}H NMR: 6.14 (1 H, d, *J* = 8.64 Hz), 6.05 (1 H, dd, *J* = 6.15 Hz, *J* = 8.75 Hz), 3.51 (3 H, s), 3.35 (1 H, m), 3.28 (1 H, dd, *J* = 3.13 Hz, *J* = 7.88 Hz), 3.19 (3 H, s), 3.09 (1 H, d, *J* = 7.88 Hz), 1.83 (2 H, m), 1.53 (2 H, m). ^{13}C NMR: 212.86, 177.17, 134.06, 130.83, 78.31, 77.36, 76.65, 54.49, 50.89, 46.03, 35.74, 28.93, 27.29, 24.18. IR (cm^{-1}): 3050, 2979, 2949, 2866, 2828, 1736, 1433, 1324, 1300, 1286, 1158, 1116. MS: *m/e* 237 (M$^+$, 42) 209 (15), 129 (42), 110 (100). Anal. Calcd for $C_{12}H_{15}NO_2S$: C, 60.73; H, 6.37. Found: C, 60.87; H, 6.41.

Formation of Adducts 11 and 12 under Perchlorate Catalysis. A solution of 6 (337 mg, 2.66 mmol) in ethereal perchlorate (10 mL, 5 M $LiClO_4$) was treated with 1-methoxy-1,3-cyclohexadiene (1.2 mL; 1.14 g, 6.58 mmol). After the solution was stirred at room temperature for 5 h, ether (40 mL) was added and the extract was washed with water (2 × 20 mL) and dried over magnesium sulfate. Evaporation of the solvent under reduced pressure gave a yellow solid. Radial chromatography on silica with hexane/chloroform (14/1) gave adduct 11 (177 mg) and adduct 12 (32 mg) in a total yield of 33%.

Adduct 13. A solution of NMM (372 mg, 3.35 mmol) in toluene (10 mL) containing 1-methoxy-1,3-cyclohexadiene (1.2 mL; 1.14 g, 6.58 mmol) was heated at 70 °C for 5 h. Evaporation of the solvent under reduced pressure, followed by radial chromatography of the residue on silica with hexane/chloroform (2:1) as eluent, gave adduct 13 (657 mg, yield 82%), mp 87–88 °C. ^{1}H NMR: 6.16–6.09 (2 H, m), 3.51 (3 H, s), 3.11 (1 H, m), 3.09 (1 H, d, *J* = 8.17 Hz), 2.96 (1 H, dd, *J* = 2.96 Hz, *J* = 8.45 Hz), 2.90 (3 H, s), 1.85–1.66 (2 H, m), 1.59–1.45 (2 H, m). IR (cm^{-1}): 3050, 2941, 2931, 1694, 1439, 1386, 1291, 1126. MS: *m/e* 221 (M$^+$, 2.81), 193 (78), 121 (41), 110 (100). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 65.22; H, 6.84.

Adduct 13 (Perchlorate Catalysis). NMM (300 mg, 2.7 mmol) was dissolved in an ethereal perchlorate solution (10 mL, 5 M, $LiClO_4$) and was treated with diene 10 (1.2 mL; 1.14 g, 6.58 mmol). The mixture was stirred at room temperature for 5 h, ether (40 mL) was added, and the solution was washed with water (2 × 20 mL), dried over magnesium sulfate, and evaporated under reduced pressure to give a yellow solid. Chromatography on silica with hexane/chloroform (2/1) gave adduct 13 (50 mg, yield 8%), the identity of which was confirmed by ^{1}H NMR and melting point.

Adduct 15. A solution of 6 (110 mg, 0.866 mmol) and 14[7] (256 mg, 0.83 mmol) in chloroform (5 mL) was heated at 60 °C under nitrogen for 5 h. Standard workup gave adduct 15 (211 mg, yield 58%) as a light yellow solid, mp 137–138 °C. ^{1}H NMR: 8.06–8.03 (m, 4 H), 7.6–7.55 (m, 2 H), 7.49–7.43 (m, 4 H), 6.16 (dt, *J* = 9.49 Hz, *J* = 2.91 Hz, 1 H), 6.09 (ddd, *J* = 9.6 Hz, *J* = 3.70 Hz, *J* = 2.18 Hz, 1 H), 5.72–5.70 (m, 1 H), 5.06 (dd, *J* = 10.99 Hz, *J* = 7.1 Hz, 1 H), 4.77 (dd, *J* = 10.97 Hz, *J* = 8.24 Hz, 1 H), 4.12 (t, *J* = 7.88 Hz, 1 H), 3.45 (dd, *J* = 8.32 Hz, *J* = 6.58 Hz, 1 H), 3.24 (s, 3 H), 3.08 (m, 1 H). ^{13}C NMR: 207.39, 177.69, 166.79, 133.25, 133.10, 130.71, 129.84, 129.72, 129.62, 129.13, 128.40, 128.39, 68.37, 64.63, 50.98, 41.05, 35.04, 29.08. MS: *m/e* 435 (M$^+$, <1), 206 (27), 191 (45), 122 (45), 105 (100). Anal. Calcd for $C_{24}H_{21}NO_5S$: C, 66.19; H, 4.86. Found: C, 66.21; H, 4.90.

Adduct 16. A solution of 14[7] (46.45 mg, 0.151 mmol) and NMM (108 mg, 0.923 mmol) in toluene (2 mL) was heated at 70 °C for 3 h. Standard workup followed by chromatography gave adduct 16 (51 mg) as a white crystalline solid, mp 152–153 °C (yield 87%). ^{1}H NMR: 8.15 (d, *J* = 0.75 Hz, 1 H), 8.13 (m, 1 H), 8.08 (d, *J* = 1.25 Hz, 1 H), 7.62–7.55 (m, 2 H), 7.50–7.43 (m, 4 H), 6.11 (dt, *J* = 9.66 Hz, *J* = 9.66 Hz, *J* = 2.64 Hz, 1 H), 6.02 (dt, *J* = 9.62 Hz, *J* = 3.03 Hz, 1 H), 5.64 (m, 1 H), 4.99 (dd, *J* = 7.15 Hz, *J* = 12.56 Hz, 1 H), 4.82 (dd, *J* = 8.29 Hz, *J* = 11.44 Hz, 1 H), 3.82 (t, *J* = 8.44 Hz, 1 H), 3.42 (dd, *J* = 6.04 Hz, *J* = 8.87 Hz, 1 H), 3.02 (s, 3 H), 2.95 (m, 1 H). MS: *m/e* 297 (M$^+$ – 122, 35), 192 (71), 175 (27), 122 (35), 105 (100). Anal. Calcd for $C_{24}H_{21}NO_6$: C, 68.73; H, 5.05. Found: C, 68.65; H, 5.10.

Ketone 19 (Hydrolyzed Product from Adduct 18). A solution of 6 (130 mg, 1.02 mmol) and *trans*-1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (0.25 mL; 0.22 g, 1.16 mmol) in toluene (15 mL) was stirred at 70 °C for 40 min. The solvent was evaporated, and the residue was chromatographed on silica, to give pure ketone 19 as a yellow crystalline solid, in 56% yield, mp 109–111 °C. ^{1}H NMR: δ 4.30 (1 H, m), 3.33 (1 H, dd, *J* = 9.24 Hz, *J* = 3.42 Hz), 3.30 (3 H, s), 3.20 (3 H, s), 3.18 (1 H, q, *J* = 9.27 Hz), 2.83 (1 H, dd, *J* = 18.35 Hz, *J* = 3.20 Hz), 2.30 (1 H, dd, *J* = 18.34 Hz, *J* = 2.19 Hz). ^{13}C NMR: 210.02, 206.28, 179.49, 77.67, 58.19, 53.34, 41.01, 37.13, 36.32, 29.25. MS: *m/e* 227 (M$^+$, 53.36), 212 (14.01), 195 (12.73), 195 (100), 142 (54.46), 127 (26.22). HRMS: calcd for $C_{10}H_{13}NO_3S$ 227.0616. Found: 227.0600.

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