Oligomerization by Triethylamine. In a typical experiment, injection of 3 μL of triethylamine caused complete oligomerization of 40 mg of CNPM in 0.5 mL of $CDCl_3$ within 15 min. The oligomer could be separated into roughly equal amounts of ether-insoluble and ether-soluble oligomers. The former showed MW ~1100 (DP ~5). The latter had MW 600–920 (DP 2–4). Their infrared spectra were identical: IR (KBr) 3067 (w), 2954 (m), 1714 (br), 1596 (sh), 1238 (br cm^{-1}); NMR ($CDCl_3$) δ 3.3–4.4 (br, 4 H), 6.7–7.7 (br, 5 H) ppm.

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A New Super-Electrophile: α-(Phenylsulfonyl)maleic Anhydride

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α-(Phenylsulfonyl)maleic anhydride is synthesized by oxidation of α-(phenylthio)maleic anhydride. The title compound reacts extremely fast with isoprene, 2,3-dimethylbutadiene, and chloroprene to form the expected [4 + 2] cycloadducts. With cyclopentadiene, the endo adduct is formed, while with furan the exo adduct is obtained in an equilibrium reaction. With p-methoxystyrene and styrene, the double Diels–Alder adducts are obtained. Determination of the rate constant for the reaction of chloroprene with α-(phenylsulfonyl)maleic anhydride proves it is more reactive than tetracyanoethylene or α-(carbomethoxy)maleic anhydride.

Introduction

1,2-Disubstituted ethylenes are rather unreactive and sluggish in cycloaddition and copolymerization reactions. Maleic anhydride, however, is reactive in these reactions; its higher reactivity is ascribed to the minimization of the steric effect by confining the two substituents into a ring and also to the planar structure that permits effective resonance stabilization of radical and anionic intermediates and favors concerted cycloadditions.[1]

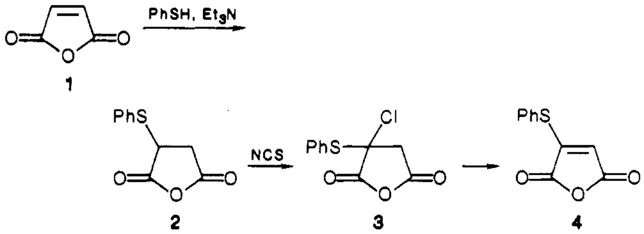
Our extensive study of the trisubstituted electrophilic ethylenes has shown that these are much more reactive than 1,2-disubstituted olefins. The unfavorable steric effects are overcome by the additional stabilization provided by the two α-substituents at the reactive center. Perfectly alternating copolymers of these trisubstituted olefins with electron-rich olefins are formed spontaneously, and cycloadducts are also frequently formed in these reactions.[2,3]

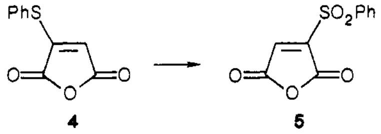
Accordingly, an electrophilically substituted maleic anhydride derivative should be especially reactive in reactions with electron-rich olefins. We have previously synthesized α-(carbomethoxy)maleic anhydride (CMA)[4] and studied its reactions with 1,3-dienes, styrenes, and vinyl ethers.[5] In these cycloaddition reactions, CMA proved to be much more reactive than tetracyanoethylene (TCNE).

In the present work, we report the synthesis and reactions of another highly electrophilic maleic anhydride derivative, namely α-(phenylsulfonyl)maleic anhydride.

Results

Synthesis of α-(Phenylsulfonyl)maleic Anhydride. α-(Phenylthio)maleic anhydride is synthesized by using literature procedures. Nucleophilic addition of thiophenol to maleic anhydride (**1**) forms the sulfide **2**,[6] which is then chlorinated to **3**.[7] Elimination to the unsaturated sulfide **4** can be achieved with triethylamine, but is more conveniently accomplished by thermal elimination of HCl.[8] Oxidation of pure **4** with m-chloroperbenzoic acid affords the desired sulfone **5** in 85% yield. An alternative procedure starts from acetylenedicarboxylic acid to which thiophenol is added in glacial acetic acid. The resulting α-(phenylthio)maleic anhydride is then oxidized using peracetic acid.[9]





α-(Phenylsulfonyl)maleic anhydride is a colorless crystalline solid, mp 170 °C, which is stable at room temperature in dry conditions.

Reactions with 1,3-Dienes. α-(Phenylsulfonyl)maleic anhydride (**5**) was reacted with isoprene, 2,3-dimethylbutadiene, and chloroprene in acetone at room temperature. The reactions were followed by NMR and TLC. The

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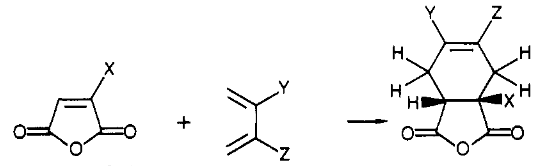
reaction with isoprene was complete in less than 3 min, while the reaction with 2,3-dimethylbutadiene was even faster, 100% cycloadduct in less than 1 min. With chloroprene, the reaction was much slower, but after 12 h, a 100% cycloadduct was obtained. The products were the expected Diels–Alder adducts **7**. In the unsymmetrical cases, only the "para" isomer formed.

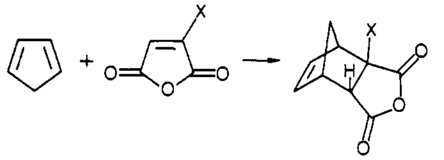


X = SPh, SO$_2$Ph **6a**: Y = CH$_3$; Z = H **7**
b: Y, Z = CH$_3$
c: Y = Cl; Z = H

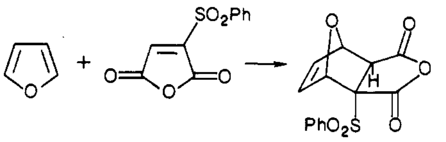
Due to the very fast reactions, only qualitative data could be obtained about the reactivity of **5** with isoprene and 2,3-dimethylbutadiene. In the case of isoprene, the reaction was *complete* in less than 3 min. This is comparable to the isoprene/CMA reaction, which has a $t_{1/2}$ of less than 1 min, and with the isoprene/TCNE reaction ($t_{1/2}$ = 5 min). α-(Phenylsulfonyl)maleic anhydride (**5**) thus appeared markedly more reactive than either CMA or TCNE.

The chloroprene/**5** cycloaddition was slow enough to be studied. A second-order reaction with a half-life of 37 min was found for the chloroprene/sulfone **5** cycloaddition in acetone-d_6 at 28 °C (concentration 0.618 M each). This corresponds to a rate constant of 6.9×10^{-4} M^{-1} s^{-1}. We can compare this to the data for chloroprene/CMA: $t_{1/2}$ = 75 min, $k_2 = 2.7 \times 10^{-4}$ M^{-1} s^{-1}.[5] The reaction of chloroprene/TCNE leads to an equilibrium and cannot be used for comparison.

Among the cyclic dienes, cyclopentadiene reacted in less than 1 min with sulfone **5** at 28 °C to yield the endo Diels–Alder adduct **8** in 100% yield. With furan on the other hand, an equilibrium is obtained after 30 min; about 50% yield of the exo adduct **10** is present in the reaction mixture.



8: X = SO$_2$Ph
9: X = SPh

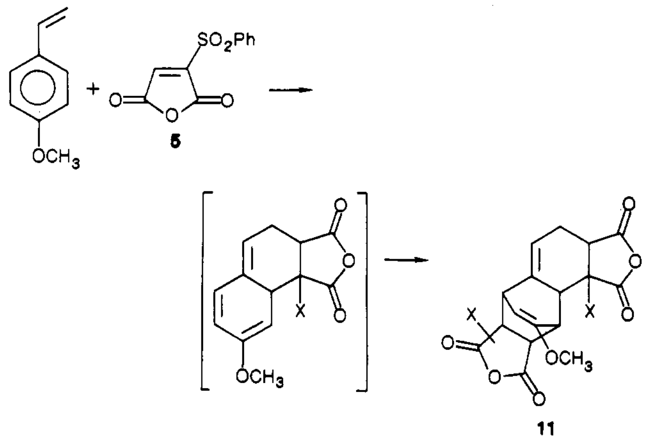


10

α-(Phenylthio)maleic anhydride (**4**) is a less reactive dienophile than maleic anhydride itself: it reacted very slowly with the most reactive diene, 2,3-dimethylbutadiene (5% yield in 24 h), and not at all with isoprene and chloroprene under our experimental conditions. With cyclopentadiene, 100% yield of endo adduct **9** was obtained in 22 h. No reaction was observed with furan.

Reaction with Styrene Derivatives. Reaction of sulfone **5** with *p*-methoxystyrene in ether at 28 °C gave high yields of the Wagner-Jauregg type adduct **11**,[10] which is formed by two consecutive Diels–Alder reactions.

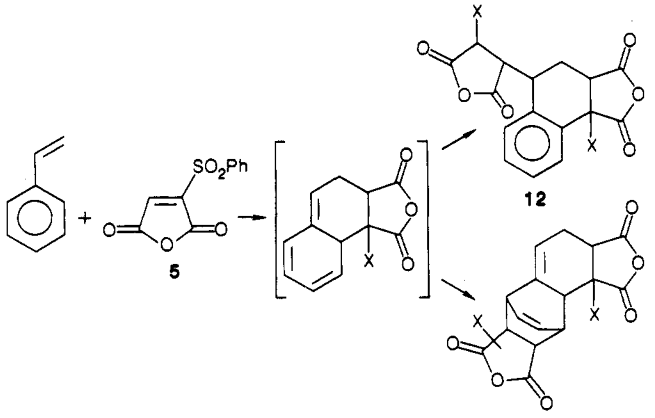
The first [4 + 2] cycloaddition of **5** with the diene composed of the exocyclic double bond and one aromatic double bond is regiospecific. The NMR spectrum is too complicated to assign the regiochemistry of the second cycloaddition. In the cycloaddition reaction of styrene



11

X = SO$_2$Ph

and **5** in acetone, both the Diels–Alder ene adduct **12** and the double Diels–Alder adduct **13** are obtained (ratio 2:1).



12

13

X = SO$_2$Ph

Discussion

In our continuing study of electrophilic olefins, α-(phenylsulfonyl)maleic anhydride was chosen, because the phenylsulfonyl substituent is very electron-withdrawing. This is shown by the Hammett constants σ_m and σ_p:[11]

COOMe	$\sigma_m = 0.35$	$\sigma_p = 0.44$
CN	$\sigma_m = 0.62$	$\sigma_p = 0.70$
SO$_2$Ph	$\sigma_m = 0.62$	$\sigma_p = 0.71$

From these values, we can conclude that SO$_2$Ph is as electrophilic as a cyano substituent and more electrophilic than a carbomethoxy group.

α-Carbomethoxymaleic anhydride, CMA, had proven to be an extremely reactive dienophile in our earlier study[4,5] and was in fact more reactive than tetracyanoethylene, TCNE.

From the [4 + 2] cycloaddition reactions with 1,3-dienes, α-(phenylsulfonyl)maleic anhydride is seen to be more reactive than CMA. This could be deduced qualitatively from the reactions with isoprene and 2,3-dimethyl-

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butadiene, which were so fast they could not be followed. Quantitative data could be obtained from the reaction with chloroprene.

With cyclopentadiene, the expected endo adduct is formed in agreement with the Alder endo rule (^1H NMR). With furan, the exo adduct is obtained (^1H NMR), similar to the MAnh–furan adduct.[12]

The high dienophilic character of sulfone **5** extended to its reactions with styrene derivatives. As described by Wagner-Jauregg in his extensive review[10] of vinyl aromatic compounds, the exocyclic ethylene moiety together with an adjacent ring "double bond" can function as a diene system; the reaction will lead to 2:1 adducts. Such 2:1 adducts were obtained in the cycloaddition of sulfone **5** to *p*-methoxystyrene and styrene. In the styrene sulfone **5** cycloaddition, the 2:1 "Diels–Alder ene" adduct **12** is also obtained, as the major product.

Experimental Section

Instrumentation. All melting points were determined on a Thomas-Hoover melting points apparatus and are uncorrected. Nuclear magnetic resonance spectra were determined on a Bruker WM-250 250-MHz spectrometer. Infrared spectra were obtained with a Perkin-Elmer 938 grating infrared spectrophotometer. Mass spectra were determined by Hewlett-Packard Model 5988A, RTE-6/VM Data System Direct Insertion Probe. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

α-(Phenylsulfonyl)maleic Anhydride (5). A solution of *m*-chloroperoxybenzoic acid (4.5 g, 26 mmol at 85%) in 50 mL of dry CH_2Cl_2 was added to a solution of α-(phenylthio)maleic anhydride (**4**) (2 g, 9.7 mmol) in 10 mL of dry CH_2Cl_2 with stirring at room temperature for half an hour. This mixture was heated at reflux while protected by a drying tube for 20 h. A heavy white solid was formed. The reaction mixture was cooled in an ice–water bath (30 min) and freed of precipitate by filtration. The filtrate was kept in freezer at −45 °C to give 1 g of a white crystalline solid: mp 168–171 °C. Hexane was added to the filtrate (the same volume of filtrate), and it was stored in freezer (−45 °C) to form some more sulfone (85% yield total).

Recrystallization with dichloromethane and hexane gave a crystalline solid: mp 172–173 °C; IR (KBr) ν_{max} 3109, 3071, 1885, 1845, 1581, 1334, 1162 cm^{-1}; ^1H NMR (acetone-*d*) δ 8.05–8.12 (m, 2 H), 8.00 (s, 1 H), 7.83–7.92 (m, 1 H), 7.72–7.84 (m, 2 H). Anal. Calcd for $C_{10}H_6O_5$ S: C, 50.42; H, 2.52; S, 13.44. Found: C, 50.39; H, 2.50; S, 13.33.

Cycloaddition Reactions of α-(Phenylthio)- and α-(Phenylsulfonyl)maleic Anhydride with 1,3-Dienes. All reactions were carried out at 28 °C with 0.5 mmol of each reagent dissolved in 1 mL of acetone. Progress of the reaction was followed by TLC. All α-(phenylsulfonyl)maleic anhydride reactions went to completion (quantitative yield), but α-(phenylthio)maleic anhydride only reacted with 2,3-dimethyl-1,3-butadiene (~5%, 24 h).

α-(Phenylsulfonyl)maleic Anhydride–2,3-Dimethyl-1,3-butadiene Adduct. The reaction was complete in less than 1 min. Recrystallization with ether/hexane gave white crystalline solid (95% yield): mp 128–129 °C; ^1H NMR ($CDCl_3$) δ 7.90–7.98 (m, 2 H), 7.76–7.83 (m, 1 H), 7.62–7.68 (m, 2 H), 4.05–4.08 (dd, *J* = 2.18, 4.37 Hz, 1 H), 2.34–2.69 (m, 4 H), 1.72 (s, 3 H), 1.62 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 19.10, 19.24 (2 CH_3), 31.51, 33.36 (2 CH_2), 42.63 (CH), 73.99 (CSO_2Ph) 125.07, 129.22 (C=C), 129.34, 130.76, 135.48 (5 CH on phenyl ring), 133.55 (C on phenyl ring), 167.71, 170.44 (2 C=O); IR (KBr) ν_{max} 1852, 1786, 1310, 1144 cm^{-1}; MS *m/e* 321 (M + 1), 179 (M − SO_2Ph).

α-(Phenylsulfonyl)maleic Anhydride–Isoprene Adduct. The reaction was complete in less than 3 min. Recrystallization with ether/hexane gave more than 90% pure crystalline solid: mp 139–142 °C IR (KBr) ν_{max} 1848, 1786, 1313, 1145; ^1H NMR ($CDCl_3$) δ 7.90–7.98 (m, 2 H), 7.76–7.84 (m, 1 H), 7.71–7.62 (m, 2 H), 5.48–5.57 (s, b, 1 H), 4.12–4.2 (dd, *J* = 2.18, 4.37 Hz, 1 H), 2.45–2.79 (m, 4 H), 1.79 (s, 3 H); MS *m/e* 307 (M + 1), 165 (M − SO_2Ph, base peak).

α-(Phenylsulfonyl)maleic Anhydride–Chloroprene Adduct. The reaction was complete in 12 h. Recrystallization with ether/hexane gave a white crystalline solid (~95%): mp 144–145 °C; IR (KBr) ν_{max} 1852, 1783, 1312, 1149 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90–7.98 (m, 2 H), 7.79–7.88 (m, 1 H), 7.62–7.71 (m, 2 H), 5.86–5.91 (m, 1 H), 4.19–4.23 (dd, *J* = 2.18, 4.37 Hz, 1 H), 2.90–3.05 (m, 2 H), 2.68–2.71 (m, 2 H); ^{13}C NMR δ 28.32, 32.20 (2 CH_2), 42.55 (CH), 72.16 (CSO_2Ph), 120.15 (C=), 129.50, 130.91, 135.85 (5 CH on phenyl ring), 132.35 (C on phenyl ring), 132.95 (C=), 167.12 (168.97) (2 C=O) MS *m/e* 327 (M + 1), 185 (M − SO_2Ph, base peak).

5-(Phenylsulfonyl)- and 5-(Phenylthio)bicyclo[2.2.1]hept-2-ene-5,6-*endo*-dicarboxylic Anhydride (8 and 9). Cyclopentadiene (0.33 mg, 0.5 mmol) was added to a solution of α-(phenylsulfonyl)- or α-(phenylthio)maleic anhydride (0.5 mmol) in 1 mL of acetone. The reactions were followed with TLC. Reactions with α-(phenylsulfonyl)maleic anhydride was complete in less than 1 min. But reaction with α-(phenylthio)maleic anhydride took 22 h. Evaporation of solvent gave an oily liquid (quantitative yield). Crystalline solids were obtained from chloroform.

5-(Phenylsulfonyl)bicyclo[2.2.1]hept-2-ene-5,6-*endo*-dicarboxylic Anhydride (8): mp 120–122 °C; IR (KBr) ν_{max} 1880, 1773, 1581, 1322, 1148 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94–8.3 (m, 2 H), 7.78–7.88 (m, 1 H), 7.62–7.73 (m, 2 H), 6.41–6.50 (m, 1 H), 6.28–6.36 (m, 1 H), 4.19–4.26 (d, 1 H), 3.62–3.70 (s, b, 1 H), 3.41–3.49 (s, b, 1 H), 2.53–2.62 (d, 1 H), 1.83–1.91 (d, 1 H); MS *m/e* 304 (M^+), 163 (M − SO_2Ph).

5-(Phenylthio)bicyclo[2.2.1]hept-2-ene-5,6-*endo*-dicarboxylic Anhydride (9): mp 83.5–85 °C; IR (KBr) ν_{max} 1879, 1778, 1566 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50–7.62 (m, 2 H), 7.36–7.49 (m, 3 H), 6.29–6.38 (m, 2 H), 3.50–3.58 (m, 1 H), 3.34–3.41 (d, 1 H), 3.21–3.28 (m, 1 H), 2.29–2.34 (m, 1 H), 1.92–2.00 (m, 1 H); MS *m/e* 272 (M^+).

5-(Phenylsulfonyl)-7-oxabicyclo[2.2.1]hept-2-ene-5,6-*exo*-dicarboxylic Anhydride (10). α-(Phenylsulfonyl)maleic anhydride (59.5 mg, 0.25 mmol) was mixed with 17 mg (0.25 mmol) of furan in 0.3 mL of deuterated acetone in NMR tube. After 30 min and 20 h, the ^1H NMR spectrum showed an equilibrium mixture 50%: ^1H NMR (acetone-*d*) δ 7.31–8.16 (m, 5 H), 6.93 (m, 1 H), 6.89 (m, 1 H), 5.30 (s, 1 H), 5.40 (d, 1 H), 3.86 (s, 1 H).

1,12-Bis(phenylsulfonyl)-7-methoxy-1,2,3,5,8,9-hexahydro-5,8-ethanonaphthalene-1,2,11,12-tetracarboxylic Dianhydride (11). *p*-Methoxystyrene (67 mg, 0.5 mmol) was added to a solution of α-(phenylsulfonyl)maleic anhydride **5** (119 mg, 0.5 mmol) in 40 mL of ether under an argon atmosphere. The solution turned yellow, but the yellow color gradually faded (15 min) and a white precipitate was formed. Filtration gave 106.6 mg (70% yield) of solid. Recrystallization with chloroform/ether gave a white crystalline solid, which decomposed at 246–248 °C: IR (KBr) ν_{max} 1858, 1787, 1635, 1315, 1150 cm^{-1}; ^1H NMR (acetone-*d*) δ 8.24–8.31 (m, 2 H), 7.77–8.09 (m, 8 H), 6.09–6.16 (m, 1 H), 5.16–5.22 (m, 1 H), 4.43–4.48 (m, 1 H), 4.22–4.28 (d, 1 H), 3.78–3.82 (d, 1 H), 3.41 (s, 3 H), 3.17–3.22 (b, 1 H), 2.79–2.91 (m, 2 H), 1.90–2.00 (m, 1 H); MS *m/e* 469 (M − SO_2Ph), 328 (M − $2SO_2Ph$).

Reaction of Styrene and α-(Phenylsulfonyl)maleic Anhydride. Styrene (52 g, 0.5 mmol) was added to a solution of α-(phenylsulfonyl)maleic anhydride (119 mg, 0.5 mmol) in 2 mL of acetone under argon atmosphere. The solution was stirred for 24 h. After removal of solvent a viscous liquid was produced. The ^1H NMR spectrum indicated the presence of Diels–Alder ene adduct **12** and Wagner-Jauregg adduct **13**: ^1H NMR δ 7.25–7.45 (phenyl from DA ene adduct **12**), 5.21–5.18 (1 H, adduct **13**), ratio 2:1 **12**:**13**; MS *m/e* 439 (M − SO_2Ph), 298 (M − $2SO_2Ph$).

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