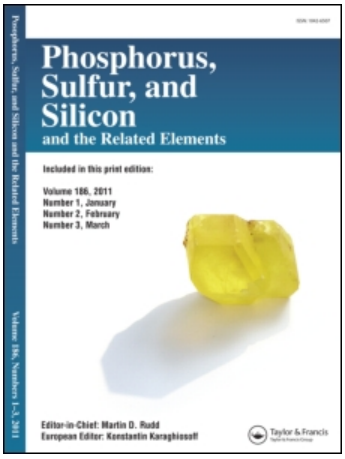

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DIELS–ALDER REACTIONS USING N-(*p*-CHLOROSULFONYLPHENYL)-MALEIMIDE AS DIENOPHILE

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N-(*p*-chlorosulfonylphenyl)maleimide reacts as a dienophile with cyclopentadiene, furan, 2,3-dimethylbutadiene, anthracene, 1,3-cyclohexadiene, 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, hexachlorocyclopentadiene and tetraphenylcyclopentadienone to give the chlorosulfonyl adducts (2, 10, 18, 24, 32, 40, 48, 56). These were converted into derivatives by reaction with amines, hydrazine and sodium azide. The stereochemistry of the Diels–Alder adducts was determined by NMR spectroscopy of the adducts and their dimethylamides; and the relative ease of addition is discussed. Attempted formation of (2) by chlorosulfonation of the adduct from N-phenylmaleimide and cyclopentadiene was unsuccessful. The spectral data are briefly discussed.

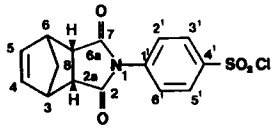
The work described forms part of our general programme on the chemistry and biological activity of aryl sulfonyl derivatives.[1–3] In particular, it extends previous studies on the reactions of N-(*p*-chlorosulfonylphenyl)maleimide (**1**) with nucleophiles.[4] In this paper, we show that (**1**) can be used as a diene in the Diels–Alder reaction without destruction of the chlorosulphonyl group so the reaction provides a useful synthetic route to novel aryl sulphonyl derivatives. The products are of interest as candidate fungicides, in view of the antifungal properties shown by cyclic imides[5–6] and sulfonamides.[7]

There are no reports of the use of (**1**) in the Diels–Alder reaction, we therefore examined the reaction of (**1**) with various dienes.

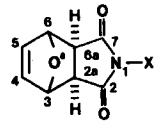
Cyclopentadiene is known[8] to be a highly reactive diene in the Diels–Alder reaction and as expected reacted with (**1**) in benzene at room temperature (30 min) to give *endo*-N-(*p*-chlorosulfonylphenyl)norbornenosuccinimide (**2**) (Chart 1). The stereochemistry of the adduct (**2**) was shown to be *endo* by comparison of the NMR spectrum with the reported data[9,10] for *endo* and *exo*-N-phenylnorbornenosuccinimides; namely the resonances for the 2a,6a-protons (δ, 3.51 *endo*, 2.87 *exo*) while those for the 3,6-protons were very similar (δ, 3.45 and 3.42 respectively). The corresponding experimental values obtained for **2** were δ 3.50 and 3.40 respectively. The stereochemistry is in agreement with the *endo*-addition rule[11] in which the reactants arrange themselves in maximum accumulation of unsaturation. The resonance for the 2a,6a-protons appears as a multiplet indicating coupling with the 3,6-protons, hence the dihedral angle between these protons must be less than 90°. If (**2**) had been *exo*, the dihedral angle would have been approximately 90° leading to virtually zero coupling.[12,13]

The adduct (**2**) was condensed with dimethylamine, aniline, hydrazine and

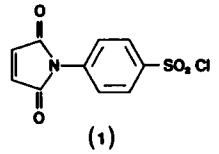
CHART 1 FORMULAE OF ADDUCTS (R–Cl) OF (1)



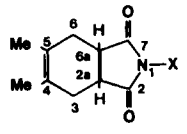
(2) = R^1Cl



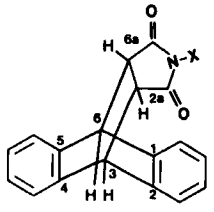
(10) = R^2Cl



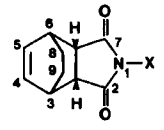
(1)



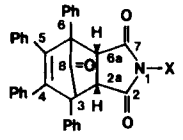
(18) = R^3Cl



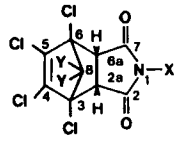
(24) = R^4Cl



(32) = R^5Cl



(56) = R^6Cl

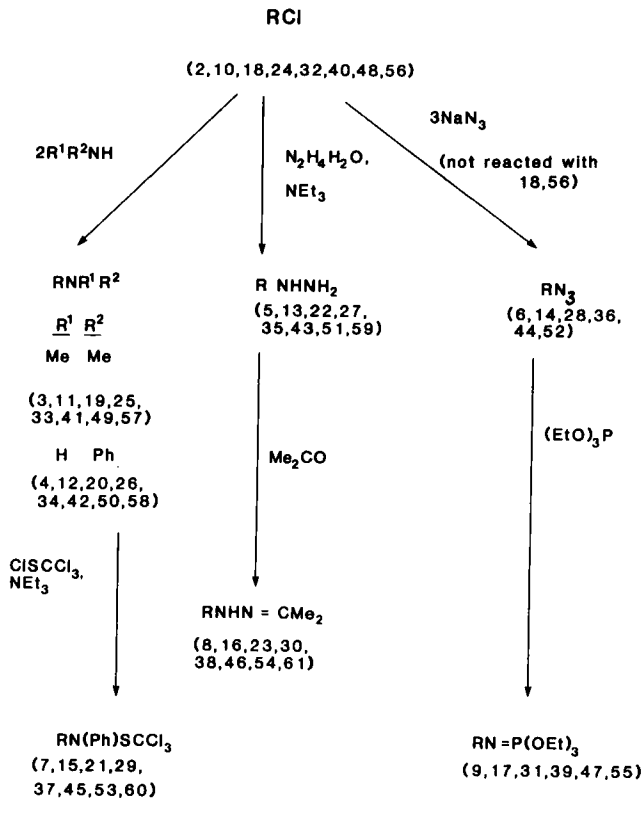


(40, Y = OMe) = R^7Cl
(48, Y = Cl) = R^1Cl

(Where X = p-$ClSO_2C_6H_4$-)

sodium azide to give the derivatives (**3–6**) (Scheme 1). The proton and carbon NMR spectra of the dimethylamide (**3**) were in good agreement with the published data[10] for *endo*-N-phenylnorbornenosuccinimide. The aromatic resonances appeared as a multiplet (δ 7.80–7.30) showing a well-defined AA'BB' pattern indicative of *p*-sulfonation. The anilide (**4**) was condensed with trichloromethanesulfonyl chloride to give **7**, such derivatives are known[14] to be fungicidal. The hydrazide (**5**) was characterized as the acetone hydrazone (**8**); the NMR spectrum showed an aliphatic:aromatic proton ratio of 14:5, in which the imidic proton appears in the aromatic multiplet. All attempts to open the imido ring of **2** by warming with excess dimethylamine or treatment with excess hydrazine were unsuccessful. The resistance of the imido ring is in marked contrast to the analogous reactions of N-(*p*-chlorosulfonylphenyl)maleimide and succinimide;[4] this may be due to the steric hindrance introduced into the system by the norborneno ring inhibiting nucleophilic attack on the carbonyl group.

A possible alternative route to **2** involved the Diels–Alder reaction of



SCHEME 1

N-phenylmaleimide and cyclopentadiene to give N-phenylnorbornenosuccinimide, followed by chlorosulfonation. However, when the adduct was heated with chlorosulfonic acid (6 equivs) at 80°C, a mixture of products resulted (4 spots on TLC). The NMR spectrum was complex and there was no olefinic proton resonance (δ 6.50), suggesting that the reagent attacked the 4,5-double bond.

Compound (**1**) reacted with furan in benzene at room temperature (12h) to give **10**. The product showed 2 spots on TLC suggesting a mixture of the *endo*- and *exo*-isomers. Condensation with dimethylamine afforded the amide (**11**), which also showed 2 spots on TLC; however recrystallization from methanol gave a compound (m.p. 167–168°C) showing one spot on TLC. To determine the stereochemistry of this product, maleic anhydride was reacted with furan as previously described[15] to give *exo*-8-oxabicyclo[2.2.1]hept-4-enosuccinic anhydride (95%). This, by successive treatment with aniline and sodium acetate–acetic anhydride, was converted into the corresponding *exo*-N-phenylsuccinimide. The NMR spectrum of the *exo*-adduct showed the resonance for the 2a,6a-protons as a singlet (δ, 3.05) as compared with δ 3.00 for the purified dimethylamide (**11**). The close agreement indicates that the latter was the

exo-isomer. The NMR spectrum of the crude compound (**11**) showed an additional four-line pattern (δ 3.75–3.65), attributed to 2a,6a-protons of the *endo*-isomer (dihedral angle less than 90°) and indicates an *exo–endo* ratio of 4:1. Molecular models of the *exo*-dimethylamide (**11**) showed that the dihedral angle between the 2a,6a and 3,6-protons was approximately 90° which explains why these protons resonate as singlets. The comparatively small difference (ca. 0.70 ppm) between the resonances of the 2a,6a-protons in the *exo*- and *endo*-isomers is probably a consequence of the shielding effect of the 4,5-double bond.[16,17] Repeated fractional recrystallization or preparative TLC was not successful isolating the *endo*-isomer; this appears to be unstable and may be in equilibrium with the reactants (retro Diels–Alder reaction), these then combine to form the more stable *exo*-isomer.[15] Compound **10** was characterized by the preparation of the derivatives (**11–17**) (Scheme 1).

Compound (**1**) reacted with 2,3-dimethylbutadiene in benzene (30 min) to give **18**; this was condensed with nucleophiles to give the derivatives (**19** to **23**) (Scheme 1). Comparison of the NMR spectrum of the dimethylamide (**19**) with that of *cis*-1,2,3,6-tetrahydrophthalimide[18] indicates that **19** possesses *cis*-stereochemistry; in agreement with the principle that the configurations of diene and dienophile are retained in the adduct.[17] The conclusion was supported by the ^{13}CNMR spectrum of **19** which showed the magnetic equivalence of the 2a,6a-carbon atoms.

Compound (**1**) was refluxed with anthracene in benzene (3h) to give **24**; this was converted into the derivatives (**25–31**) (Scheme 1). The NMR spectrum of the dimethylamide (**25**) confirmed the structure as the 3,6-adduct. The 3,6 and 2a,6a-protons resonated as two multiplets (δ 4.95–4.80 and 3.50–3.40 respectively) and the chemical shifts were in good agreement with the reported[19] data for N-phenyldibenzobicyclo[2.2.1]octanosuccinimide. Diels and Alder predicted[20] 9,10-addition; this conclusion is supported by frontier orbital considerations[21] and the absence of olefinic proton resonances in the NMR spectrum of **25** excluded the possibility of 1,4-addition. In the reactions of **24** with aniline and hydrazine methanol was not a satisfactory solvent and had to be replaced by acetone or THF to obtain the derivatives **26** and **27**. The failure of these condensations in methanol is probably due to a combination of poor solubility and reduced nucleophilicity in the polar protic solvent.

Compound (**1**) reacted with 1,3-cyclohexadiene in benzene at room temperature (3h) to give **32**; 1,3-cyclohexadiene was less reactive than cyclopentadiene probably due to the larger distortion energy required to build up the transition state between diene and dienophile as compared with the cyclopentadiene analogue.[22] We conclude that the **32** is the *endo*-isomer, because in the NMR spectrum of the dimethylamide (**33**), the resonance for the 2a,6a-protons (δ 3.40–3.25) was very similar to that obtained for *endo*-bicyclo[2.2.2]oct-4-enosuccinic anhydride[22] (see p. 74).

1 was refluxed with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene in benzene (8h) to give **40**, which was converted into the derivatives (**41–47**) (Scheme 1). The reduced reactivity of this diene in the Diels–Alder reaction is probably a consequence of dipole–dipole repulsion between the two polar reactants.[23] The NMR spectrum of the dimethylamide (**41**) was determined in the presence of tris-

6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionatoeuropium[Eu(fod)$_3$)]. If complexation of the reagent occurred with the methoxy oxygen atoms, the stereochemistry can be determined because the chemical shift of the 2a,6a-protons would only be altered if they had the *exo*-configuration. The procedure, unfortunately, was unsuccessful because the europium salt complexed preferentially with the oxygen atoms of the sulfonyl group.

1 by refluxing with hexachlorocyclopentadiene in *o*-xylene (16h) formed the adduct (**48**); the addition was much slower than the other Diels–Alder reactions, probably due to increased dipole–dipole repulsion between the reactants. **48** was converted into the derivatives (**49–55**) (Scheme 1). In the NMR spectrum of the dimethylamide (**49**), the resonance for the 2a,6a-protons appeared at δ 4.10 which was identical to the reported data[24] for the chemical shift of the 1,2-*exo*-protons in *endo* 3,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-4-enosuccinic acid. This clearly implies that the dimethylamide (**49**) must have the *endo*-configuration. By analogy with this compound, we conclude that **41** is also the *endo*-isomer.

Compound (**1**) was refluxed with tetraphenylcyclopentadienone in benzene (8h) to give **56**, which was characterized as the derivatives (**57–61**) (Scheme 1). Attempts to obtain the azide by reaction with sodium azide in acetone or methanol were unsuccessful. The NMR spectra of the dimethylamide (**57**) and the acetone hydrazone (**61**) showed the 2a,6a-proton resonances (δ 4.40, 4.30 respectively); these were in excellent agreement with the reported data[25] for *endo*-N-phenyl-8-oxo-3,4,5,6-tetraphenylbicyclo[2.2.1] hept-4-eno succinimide.

The IR spectra of the compounds generally exhibited the two carbonyl absorption bands (1780, 1720 cm^{-1}) characteristic of cyclic imides,[26a] together with the symmetric and asymmetric stretching absorptions (1340, 1160 cm^{-1}) for the sulfonyl group.[26b].

In the mass spectra, the majority of the compounds showed the molecular ions (M^+) (Table I). Notable exceptions were the hydrazides and hydrazones which

TABLE I

Physical data for the adducts and derivatives

Compound	M.p. °C	Yield (%)	Molecular formula	Elementary analysis %[a] C	H	N		MS M^+
2	209–210	90	$C_{15}H_{12}ClNO_4S$	52.9 (53.3)	3.3 (3.5)	4.3 (4.1)		339, 337
3	187	78	$C_{17}H_{18}N_2O_4S$	58.7 (59.0)	5.3 (5.2)	8.1 (8.1)		346
4	195–196	75	$C_{21}H_{18}N_2O_4S$	64.1 (63.95)	4.8 (4.6)	6.9 (7.1)		394
5	170	50	$C_{15}H_{15}N_3O_4S$	53.8 (54.05)	4.3 (4.5)	12.8 (12.6)		—
6	>340	76	$C_{15}H_{12}N_4O_4S$	52.0 (52.3)	3.5 (3.5)	16.2 (16.3)		344
7	181–182	68	$C_{22}H_{17}Cl_3N_2O_4S_2$	48.2 (48.6)	3.2 (3.1)	4.9 (5.2)	S, 11.6 (S, 11.8)	551[b]
8	169–170	70	$C_{18}H_{19}N_3O_4S$	57.6 (57.9)	5.2 (5.1)	11.0 (11.3)		—
9	117–118	89	$C_{21}H_{27}N_2O_7PS$	52.1 (52.3)	5.7 (5.6)	5.9 (5.8)		482

Table I (*contd*)

Compound	M.p. °C	Yield (%)	Molecular formula	Elementary analysis %[a] C	H	N		MS M^+
10	140–142	80	$C_{14}H_{10}ClNO_5S$	49.3 (49.5)	3.0 (2.9)	4.3 (4.1)		273, 271 ($M-C_4H_4O$)
11	167–168	70	$C_{16}H_{16}N_2O_5S$	55.4 (55.2)	4.6 (4.6)	8.0 (8.0)		280 ($M-C_4H_4O$)
12	156	70	$C_{20}H_{17}N_2O_5S$	60.1 (60.4)	4.5 (4.3)	7.0 (7.05)		329 ($M-C_4H_4O$)
13	210–212	72	$C_{14}H_{13}N_3O_5S$	49.8 (50.1)	4.1 (3.9)	12.3 (12.5)		—
14	146	78	$C_{14}H_{10}N_4O_5S$	48.3 (48.5)	3.1 (2.9)	15.9 (16.2)		274 ($M-C_4H_4O$)
15	136–137	75	$C_{21}H_{15}Cl_3N_2O_5S_2$	46.1 (46.2)	2.7 (2.7)	4.7 (5.1)	S, 11.6 (S, 11.7)	482 ($M-C_4H_4O$)
16	172–173	76	$C_{17}H_{17}N_3O_5S$	54.2 (54.4)	4.7 (4.5)	11.0 (11.2)		—
17	162	85	$C_{20}H_{25}N_2O_8PS$	49.3 (49.6)	5.0 (5.2)	5.4 (5.8)		—
18	141–142	80	$C_{16}H_{16}ClNO_4S$	54.1 (54.3)	4.6 (4.5)	4.2 (4.0)		355, 353
19	166	85	$C_{18}H_{22}N_2O_4S$	59.3 (59.7)	6.1 (6.1)	7.5 (7.7)		362
20	178	76	$C_{22}H_{22}N_2O_4S$	64.2 (64.4)	5.6 (5.4)	7.0 (6.8)		410
21	162–163	85	$C_{23}H_{21}Cl_3N_2O_4S_2$	49.1 (49.3)	3.7 (3.8)	4.9 (5.0)	S, 11.4 (S, 11.4)	564[b]
22	Oil	70	$C_{16}H_{17}N_3O_4S$	55.0 (55.3)	4.8 (4.9)	12.0 (12.1)		—
23	210–211	60	$C_{19}H_{23}N_3O_4S$	58.5 (58.6)	6.0 (5.9)	10.6 (10.8)		—
24	275–276	82	$C_{24}H_{16}ClNO_4S$	63.8 (64.1)	3.4 (3.5)	3.0 (3.1)		451, 449
25	316	80	$C_{26}H_{22}N_2O_4S$	67.7 (68.1)	4.8 (4.8)	6.0 (6.1)		458
26	281–282	80	$C_{30}H_{22}N_2O_4S$	70.8 (71.1)	4.5 (4.35)	5.4 (5.5)		506
27	274	91	$C_{24}H_{19}N_3O_4S$	64.4 (64.7)	4.4 (4.3)	9.6 (9.4)		—
28	195–196	84	$C_{24}H_{16}N_4O_4S$	67.1 (67.3)	6.8 (7.1)	6.6 (6.5)		428
29	247–248	70	$C_{31}H_{21}Cl_3N_2O_4S_2$	56.7 (56.8)	3.2 (3.2)	4.1 (4.3)	S, 9.6 (S, 9.8)	650[b]
30	300	60	$C_{27}H_{23}N_3O_4S$	66.5 (66.8)	4.9 (4.7)	8.5 (8.7)		—
31	327–328	65	$C_{30}H_{31}N_2O_7PS$	60.3 (60.6)	5.1 (5.2)	4.8 (4.7)		594
32	270	85	$C_{16}H_{14}ClNO_4S$	54.4 (54.6)	3.8 (4.0)	4.1 (4.0)		353, 351
33	233–234	70	$C_{18}H_{20}N_2O_4S$	59.9 (60.0)	5.5 (5.6)	7.8 (7.8)		360
34	224	96	$C_{22}H_{20}N_2O_4S$	65.0 (64.7)	4.8 (4.9)	7.0 (6.9)		408
35	190–191	73	$C_{16}H_{17}N_3O_4S$	55.0 (55.3)	5.1 (4.9)	12.0 (12.1)		—
36	189–190	80	$C_{16}H_{14}N_4O_4S$	53.3 (53.6)	3.6 (3.9)	15.4 (15.6)		—
37	174–175	65	$C_{23}H_{19}Cl_3N_2O_4S$	49.3 (49.5)	3.5 (3.4)	5.1 (5.0)		562[b]

Table I (*contd*)

Compound	M.p. °C	Yield (%)	Molecular formula	Elementary analysis %[a] C	H	N		MS M^+
38	124	94	$C_{19}H_{21}N_3O_4S$	59.0 (58.9)	5.4 (5.4)	11.0 (10.9)		—
39	137–138	70	$C_{22}H_{29}N_2O_7PS$	53.1 (53.2)	6.0 (5.8)	5.5 (5.6)		—
40	235–236	91	$C_{17}H_{12}Cl_5NO_6S$	37.8 (38.1)	2.4 (2.2)	2.7 (2.6)		543[b]
41	305–306	93	$C_{19}H_{18}Cl_4N_2O_6S$	41.7 (41.9)	3.2 (3.3)	5.1 (5.1)		513[b] (M-Cl)
42	244	92	$C_{23}H_{18}Cl_4N_2O_6S$	46.4 (46.6)	2.8 (3.0)	4.8 (4.7)		592[b]
43	201–202	70	$C_{17}H_{15}Cl_4N_3O_6S$	38.6 (38.4)	2.6 (2.8)	7.9 (7.9)		—
44	196–197	80	$C_{17}H_{12}Cl_4N_4O_6S$	37.8 (37.6)	2.4 (2.2)	10.3 (10.3)		542[b]
45	173–174	82	$C_{24}H_{17}Cl_7N_2O_6S_2$	39.1 (38.8)	2.4 (2.3)	3.9 (3.8)		—
46	229–230	81	$C_{20}H_{19}Cl_4N_3O_6S$	42.1 (42.0)	3.3 (3.3)	7.3 (7.4)		—
47	140–141	88	$C_{23}H_{27}Cl_4N_2O_9PS$	40.8 (40.6)	3.8 (4.0)	4.0 (4.1)		686[b]
48	276	60	$C_{15}H_6Cl_7NO_4S$	32.8 (33.05)	1.3 (1.1)	2.9 (2.6)		555[b]
49	320	80	$C_{17}H_{12}Cl_6N_2O_4S$	37.1 (36.9)	2.2 (2.2)	5.3 (5.1)	S, 12.3 (S, 12.9)	562[b]
50	222	94	$C_{21}H_{12}Cl_6N_2O_4S$	42.0 (41.9)	1.9 (2.0)	4.8 (4.7)		610[b]
51	130–131	60	$C_{15}H_9Cl_6N_3O_4S$	33.4 (33.3)	1.6 (1.7)	7.8 (7.8)		—
52	187–188	89	$C_{15}H_6Cl_6N_4O_4S$	33.0 (32.7)	1.1 (1.1)	10.3 (10.2)		563[b]
53	135	78	$C_{22}H_{11}Cl_9N_2O_4S_2$	35.1 (35.2)	1.4 (1.5)	3.8 (3.7)		—
54	215–216	77	$C_{18}H_{13}Cl_6N_3O_4S$	37.0 (37.2)	2.1 (2.2)	7.0 (7.2)		—
55	256–257	80	$C_{21}H_{21}Cl_6N_2O_7PS$	36.3 (36.6)	3.1 (3.0)	3.9 (4.1)		698[b]
56	239–240	83	$C_{39}H_{26}ClNO_5S$	71.1 (71.4)	3.8 (4.0)	2.3 (2.1)		628, 626 (M-CO)
57	229	80	$C_{41}H_{32}N_2O_5S$	73.9 (74.1)	4.8 (4.8)	4.1 (4.2)		636 (M-CO)
58	224	80	$C_{45}H_{32}N_2O_5S$	75.6 (75.8)	4.3 (4.5)	4.0 (3.9)		684 (M-CO)
59	215–216	80	$C_{39}H_{29}N_3O_5S$	72.0 (71.9)	4.5 (4.45)	6.5 (6.45)		623 (M-CO)
60	192	78	$C_{46}H_{31}Cl_3N_2O_5S_2$	64.1 (64.1)	3.8 (3.6)	3.2 (3.3)		—
61	191–192	70	$C_{42}H_{33}N_3O_5S$	72.7 (72.9)	4.8 (4.8)	6.1 (6.1)		—

[a] Calculated values in parenthesis.
[b] Molecular ion cluster, highest ion quoted.

suffered extensive fragmentation, in agreement with previous observations.[1,27] The furan derivatives (**10–17**) also failed to give molecular ions and loss of the furan moiety occurred, while the 8-oxo compounds (56–60) eliminated carbon monoxide (Table I).

In the NMR spectra of the acetone hydrazones the methyl protons of the N=CMe_2 group resonated as two singlets, indicating that they were magnetically non-equivalent.

EXPERIMENTAL

Elemental analyses were carried out by ICI Ltd (Pharmaceuticals Division, Alderley Park, Cheshire, England. Melting points were determined with a Gallenkamp electric apparatus and are uncorrected. IR spectra were measured as Nujol mulls on a Unicam SP 1000 spectrophotometer. NMR spectra were recorded on Burker WP 80 spectrometer using TMS as internal standard (s = singlet, d = doublet, dd = double doublet, m = multiplet, t = triplet, q = quartet), an asterisk indicates a signal that is removed by D_2O treatment. TLC was carried out using Camlab Polygram silica gel plates sensitized to UV 254 nm.

The Diels–Alder additions

N-(p-chlorosulfonylphenyl)norbornenosuccinimide (**2**). Cyclopentadiene (2.9 g) was added to a solution of N-(*p*-chlorosulfonylphenyl)maleimide (**1**, 7.0 g) in benzene (30 ml) at room temperature. After 30 min, petroleum ether (70 ml) was added; the precipitate was filtered off, washed with petroleum ether (2 × 20 ml) and dried to give **2**. TLC (EtOAc-cyclohexane 1:1) showed one spot, R_F 0.33. IR: 1780, 1720 (CO), 1600 (ArC=C), 1350, 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.10–7.60 (m, 4H, ArH), 6.30 (t, 2H, 4,5-H), 3.50, 3.40 (2m, 4H, 2a, 6a-H, 3, 6-H), 1.80–1.60 (q, 2H, 8-H).

endo-N-Phenylnorbornenosuccinimide. This was prepared similarly by reaction of cyclopentadiene and N-phenylmaleimide. Yield (85%), m.p. 139–140°C (lit.[9] 140–141°C). NMR ($CDCl_3$) δ: 7.30–7.0 (m, 5H, ArH), 6.30 (m, 2H, 4,5-H), 3.51, 3.45 (2m, 4H, 2a, 6a-H, 3, 6-H), 1.80–1.60 (q, 2H, 8-H).

exo-N-(p-chlorosulfonylphenyl)-8-oxobicyclo[2.2.1]hept-4-eno succinimide (**10**). Furan (50 g) was reacted with compound **1** (21 g) in benzene (30 ml) for 12 h at room temperature to give compound (10). TLC (EtOAc-cyclohexane 4:1) showed two spots, R_F 0.68, 0.50. IR: 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

exo-N-phenyl-8-oxabicyclo[2.2.1]hept-4-eno succinimide. Furan reacted similarly with maleic anhydride to give the *exo*-succinic anhydride (95%), m.p. 122–123°C (lit.[15] 125°C). The product, by treatment with aniline followed by heating with acetic anhydride–sodium acetate, afforded the title compound (60%), m.p. 164–165°C (lit.[28] 165.5). IR: 1780, 1720 (C=O), 1600 (ArC=C) cm^{-1}. NMR ($CDCl_3$) δ: 7.50–7.35 (m, 5H, ArH), 6.50 (s, 2H, 4,5-H), 5.3 (s, 2H, 3,6-H), 3.05 (s, 2H, 2a,6a-H). ^{13}CNMR ($CDCl_3$) δ: 175.6 (2,7-C), 136.9 (4,5-C), 132.0–126.8 (ArC), 81.7 (3,6-C) 47.8 (2a, 6a-C).

N-(p-Chlorosulfonylphenyl)-cis-1,2,3,6-4,5-dimethylphthalimide (**18**). Compound (**1**, 13.5 g) was reacted with 2,3-dimentylbutadiene (6.1 g) in benzene (30 ml) for 30 min at room temperature to give **18**. IR: 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

N-(p-Chlorosulfonylphenyl)dibenzobicyclo[2.2.2]octano-succinimide (**24**). The sulphonyl chloride (**1**, 5 g) was refluxed with anthracene (3.3 g) in benzene (75 ml) for 3h. The solution, on cooling, gave 24. TLC (EtOAc-cyclohexane 1:3) showed one spot, R_F 0.25. IR: 1780, 1730 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

N-(p-Chlorosulfonylphenyl)bicyclo[2.2.2]oct-4-eno succinimide (**32**). Compound **1** (13.5 g) was reacted with 1,3-cyclohexadiene (6 g) in benzene (30 ml) for 3h to give 32. TLC (EtOAc-cyclohexane 1:1) showed one spot, R_F 0.48. IR: 1780, 1715 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

N-(p-Chlorosulfonylphenyl)-3,4,5,6-tetrachloro-8,8-dimethoxybicyclo[2.2.1]hept-4-eno succinimide (**40**). Compound (**1**, 40 g) was refluxed with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (50 g)

in benzene (50 ml) for 8h. The solvent was evaporated under reduced pressure and the residue washed with petroleum ether (3 × 10 ml) to give 40. TLC (EtOAc-cyclohexane 1:1) showed one spot, R_F 0.55. IR: 1780, 1730 (C=O), 1600 (ArC=C), 1340, 1180 (SO_2) cm^{-1}.

N-(p-Chlorosulfonylphenyl)-3,4,5,6,8,8-hexachlorobicyclo[2.2.1]hept-4-eno succinimide (**48**). Compound **1** (2.5 g) was refluxed with hexachlorocyclopentadiene (2.8 g) in *o*-xylene (30 ml) for 16h. The solution was cooled, diluted with petroleum ether (50 ml) and the precipitate filtered off to give **48**. TLC (EtOAc-cyclohexane 1:1) gave one spot, R_F 0.62. IR: 1780, 1735 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

N-(p-chlorosulfonylphenyl)-8-oxo-3,4,5,6-tetraphenylbicyclo[2.2.1]hept-4-eno succinimide (**56**). Compound **1** (5.0 g) was refluxed with tetraphenylcyclopentadienone (7.1 g) in benzene (60 ml) for 8h to give **56**. TLC (EtOAc-cyclohexane) showed one spot, R_F 0.70. IR (KBr) 1785, 1720 (C=O), 1600 (ArC=C), 1340, 1170 (SO_2) cm^{-1}.

General procedures for the Synthesis of Sulphonyl Derivatives

Dimethylamides (**3**, **11**, **19**, **25**, **33**, **41**, **49**, **57**). Dimethylamine 30% aq. solution (0.02 mol) was added to a stirred mixture of the sulfonyl chloride (0.01 mol) in methanol (30 ml) at 0°C. The mixture was left at room temperature for 2h and was poured onto ice-water (50 ml). The precipitate was collected, washed with water and purified by recrystallization from methanol.

Compound (**3**). IR: 1780, 1720 (C=O), 1600 (ArC=C), 1360, 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 7.80–7.30 (m, 4H, ArH), 6.20 (t, 2H, 4,5-H), 3.50-3.45 (2m, 4H, 2a, 6a-H, 3,6-H), 2.70 (s, 6H, Me), 1.90–1.50 (q, 2H, 8-H). ^{13}C NMR ($CDCl_3$) δ: 176.3 (2, 7-C), 136.01 (1',4'-C), 134.9 (4,5-C), 128.65 (2',6'-C), 127.1 (3',5'-C), 52.5 (8-C), 46.1 (3,6-C), 45.8 (2a,6a-C).

Compound **11**. Crude product, m.p. 148–152°C. TLC (EtOAc-cyclohexane 3:1) showed two spots, R_F 0.36, 0.24. Recrystallization (methanol) gave pure **11**. TLC, one spot, R_F 0.24. IR: 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 7.90–7.30 (m, 4H, ArH), 6.60 (s, 2H, 4,5-H), 5.40 (s, 2H, 3,6-H), 3.00 (s, 2H, 2a, 6a-H), 2.65 (s, 6H, Me). ^{13}C NMR ($CDCl_3$) δ: 174.8 (2, 7-C), 136.8 (4, 5-C), 136.1 (1'-C), 135.6 (4'-C), 128.6 (2',6'-C), 126.9 (3',5'-C), 81.7 (3,6-C), 47.7 (2a,6a-C), 37.9 (Me).

Compound **19**. NMR ($CDCl_3$) δ: 7.90–7.45 (m, 4H, ArH), 3.30–3.15 (m, 2H, 2a,6a-H), 2.75 (s, 6H, NMe), 2.60–2.40 (m, 4H, 3,6-H), 1.70 (s, 6H, Me). ^{13}C NMR ($CDCl_3$) δ: 178.9 (2,7-C), 136.3 (1'-C), 135.4 (4'-C), 128.6 (2',6'-C), 127.3 (4,5-C), 126.8 (3',5'-C), 40.3 (2a,6a-C), 37.9 (NMe), 31.3 (3.6-C), 19.4 (Me).

Compound **25**. NMR ($CDCl_3$) δ: 7.80–6.80 (m, 12H, ArH), 4.95–4.80 (m, 2H, 3,6-H), 3.50–3.40 (m, 2H, 2a,6a-H), 2.70 (s, 6H, Me).

Compound **33**. NMR ($CDCl_3$) δ: 7.80–7.40 (m, 4H, ArH), 6.35–6.20 (m, 2H, 4,5-H), 3.40–3.25 (m, 2H, 2a,6a-H), 3.10–3.00 (m, 2H, 3,6-H), 2.80 (s, 6H, Me), 1.80–1.55 (m, 4H, 8,9-H).

Compound **41**. NMR ($CDCl_3$): δ: 8.00–7.30 (m, 4H, ArH), 3.85 (s, 2H, 2a,6a-H), 3.70, 3.60 (2s, 6H, OMe), 2.60 (s, 6H, Me). NMR ($CDCl_3$-Eu (fod)$_3$, 20 mg) δ: 8.95–7.60 (m, 4H, ArH), 4.05 (s, 2H, 2a,6a-H), 3.75, 3.65 (2s, 6H, OMe), 3.45 (s, 6H, Me).

Compound **49**. IR: 1780, 1735 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.00–7.30 (m, 4H, ArH), 4.10 (s, 2H, 2a,6a-H), 2.80 (s, 6H, Me); with Eu (fod)$_3$ (20 mg): 9.15–7.60 (m, 4H, ArH), 4.20 (s, 2H, 2a,6a-H), 3.60 (s, 6H, Me).

Compound **57**. IR (KBr): 1785 (C=O), 1720 (CON), 1600 (ArC=C), 1340, 1170 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.00–6.60 (m, 24H, ArH), 4.40 (s, 2H, 2a,6a-H), 2.75 (s, 6H, Me).

Anilides (**4**, **12**, **20**, **26**, **34**, **42**, **50**, **58**). These were prepared similarly to the dimethylamides, except for an increased reaction time (6h); for compound **26**, acetone had to be used as solvent. Some illustrative spectra are given below:
20 IR: 3280 (NH), 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. MS: 410 (M^+), 318 (M-NHPh), 254 (M-SO_2NHPh), 172 (M-SO_2NHPh,-C_6H_{10}), 118, 107 (PhNCO), 93 (PhNH), 82.
58 IR (KBr): 3250 (NH), 1780 (C=O, ketone), 1720 (CON), 1600 (ArC=C), 1340, 1170 (SO_2) cm^{-1}.

Hydrazides (**5**, **13**, **22**, **27**, **35**, **43**, **51**, **59**). These were prepared by addition of a solution of hydrazine hydrate 98% (0.02 mol) and triethylamine (0.02 mol) to a stirred suspension of the appropriate sulfonyl chloride (0.02 mol) in methanol at 0°C. The mixture was left at room temperature (5h) and poured onto ice-water. The precipitate was filtered off, washed with water and dried in a vacuum desiccator to give the products. For example, compound **5**:
IR: 3380, 3260 (NH), 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.
The hydrazides were refluxed with acetone (15 ml) for 15 min followed by 45 min at room temperature to give the *acetone hydrazones* (**8**, **16**, **23**, **30**, **38**, **46**, **54**, **61**).

Compound **8**. IR: 3220 (NH), 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.00–7.30 (m, 5H, ArH, NH), 6.20 (s, 2H, 4,5-H), 3.50 (s, 4H, 2a,6a-H, 3,6-H), 2.00, 1.80 (2s, 6H, Me).

Compound **30**. IR: 3160 (NH), 1780, 1720 (C=O), 1600 (ArC=C), 1345, 1160 (SO_2) cm^{-1}. NMR (DMSO-d_6) δ: 10.10* (s, 1H, NH), 7.90–6.70 (m, 12H, ArH), 4.95–4.80 (m, 2H, 3,6-H), 3.50–3.40 (m, 2H, 2a,6a-H), 1.85, 1.80 (2s, 6H, Me).

Compound **61**. IR (KBr): 3240 (NH), 1780 (C=O, ketone), 1720 (CON), 1600 (ArC=C), 1340, 1170 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.10–6.60 (m, 25H, ArH, NH), 4.30 (s, 2H, 2a,6a-H), 1.90, 1.75 (2s, 6H, Me).

N-(Trichloromethylsulfonyl) derivatives (**7**, **15**, **21**, **29**, **37**, **45**, **53**, **60**). These were obtained by addition of a solution of trichloromethylsulfonyl chloride (0.01 mol) and triethylamine (0.01 mol) in ether (25 ml) to a stirred suspension of the sulfonanilide (0.005 mol) in ether (25 ml) at room temperature. The mixture was stirred for 2h, the ether removed *in vacuo* and the solid residue washed with water. The products were purified by recrystallization from acetone.

Compound **7**. IR: 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}.

Compound **60**. IR (KBr): 1780 (C=O, ketone), 1720 (CON), 1600 (ArC=C), 1340, 1170 (SO_2) cm^{-1}.

Azides (**6**, **14**, **28**, **36**, **44**, **52**). These were prepared by reaction of the sulfonyl chloride (0.01 mol) with sodium azide (0.03 mol) in aqueous acetone at room temperature (1h). The mixture was poured onto crushed ice; the precipitate collected, washed with water, and recrystallized (acetone).

Compound **6**. IR: 2100 (N_3), 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. The azides (0.005 mol) by reaction with triethylphosphite (0.005 mol) in toluene (20 ml) at room temperature (15 min) gave the corresponding triethoxyphosphinimines (**9**, **17**, **31**, **39**, **47**, **55**).

Compound **9**. IR: 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1165 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.00–7.30 (m, 4H, ArH), 6.30 (s, 2H, 4,5-H), 4.30–4.10 (m, 6H, $O\underline{CH_2}CH_3$), 3.50 (s, 4H, 2a,6a-H, 3,6-H), 1.80–1.60 (q, 2H, 8-H), 1.50–1.30 (t, 9H, $OCH_2\underline{CH_3}$). MS: 482 (M^+), 316 (M-P $(OEt)_3$), 238 (M-$SO_2NP(OEt)_3$), 200, 172, 144, 118, 116, 91, 66.

Compound **17**. IR: 1780, 1720 (C=O), 1600 (ArC=C), 1340, 1160 (SO_2) cm^{-1}. NMR ($CDCl_3$) δ: 8.15–7.35 (m, 4H, ArH), 6.60–6.50 (dd, 2H, 4,5-H), 5.40–5.30 (dd, 2H, 3,6-H), 4.45–4.00 (m, 6H, $O\underline{CH_2}CH_3$), 3.00 (s, 2H, 2a,6a-H), 1.50–1.20 (t, 9H, $OCH_2\underline{CH_3}$).

endo-Bicyclo[2.2.2]oct-4-eno succinic anhydride. 1,3-cyclohexadiene (4.1 g) was reacted with maleic anhydride (5.0 g) in benzene (50 ml) at room temperature for 3h. The solvent was removed under reduced pressure and the residue washed with water. Recrystallization from ether gave the anhydride (70%), m.p. 146–147°C (lit.[22] 146–147°C). NMR ($CDCl_3$) δ: 6.40–6.25 (m, 2H, 4,5-H), 3.40–3.20 (m, 2H, 2a,6a-H), 3.10–3.00 (m, 2H, 3,6-H), 1.80–1.25 (m, 2H, 8,9-H). We thank the British Council and the Brazilian Government for a Research Award (RN) and ICI Ltd (Pharmaceuticals Division) for microanalyses.

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