Thermal Cycloaddition of *N*-Arylmaleimides to Phenols: the Convenient Synthesis of Bicyclo[2.2.2]oct-2-en-5-one and Tricyclo[3.3.0.0^{2,8}]octan-2-one Derivatives from Phenols

Derek Bryce-Smith, Andrew Gilbert, Ian S. McColl and (in part) Michael G. B. Drew, and Paul Yianni
Department of Chemistry, University of Reading, Whiteknights, PO Box 224, Reading, Berkshire, RG6 2AD

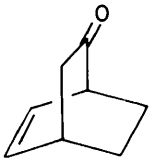
Monohydric phenols undergo 2,5-thermal cycloaddition of N-substituted maleimides to give bicyclo[2.2.2]oct-2-en-5-ones. Homopolymers of the maleimides are also concurrently formed, except in the case of *N*-(2,6-dimethylphenyl)maleimide: this is the preferred addend and gave a 63% yield of the 2,5-adduct as a mixture of *exo* and *endo* isomers. U.v. irradiation in acetone of the diester (**16**) derived from the *endo* adduct of phenol and *N*-phenylmaleimide gave the tricyclo[3.3.0.0^{2,8}]octan-3-one (**17**) in quantitative yield.

Compounds incorporating the bicyclo[2.2.2]oct-2-en-5-one unit (**1**) have been elegantly shown by Schaffner *et al.* to be useful starting materials for transformations leading to polycyclopentanoid terpenes and prostacyclin analogues.[1] The most direct synthesis of this type of structure would be by Diels–Alder addition of a dienophile to phenol, but literature reports of thermal 1,4-cycloadditions to the benzene ring are extremely sparse and in most cases the product yields are so poor that the reactions are of theoretical rather than synthetic interest. Reported additions to benzenoid compounds include dicyanoacetylene to benzene (14% yield)[2] and durene,[3] and hexafluorobut-2-yne to durene (40%).[4] Maleic anhydride does not undergo thermal cycloaddition to benzene (the photoaddition is well known[5]) but adds inefficiently to naphthalene (5.2% yield).[6] Although it has been reported to form the thermal 1,4-cycloadduct (**2**) (4—10% yield) with hydroquinone[7,8] and an analogous adduct with 2,5-dimethylhydroquinone,[9] the reaction with dihydric phenols is not widely applicable, and there have been no reports of corresponding additions to monohydric phenols. Thus resorcinol and pyrocatechol are unreactive,[9] and substituent effects of alkyl groups in the quinol series appear in general to be sterically inhibiting rather than electronically assisting.

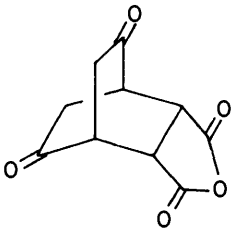
Despite such discouraging literature, we considered the one-step route to compounds of type (**1**) *via* thermal cycloaddition of a dienophile to a phenol so potentially advantageous that we have investigated its feasibility in detail.[10]

Results and Discussion

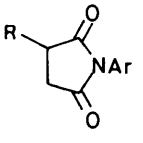
Mass spectral evidence was obtained for the formation of 1:1 adducts of phenol and maleic anhydride but yields were low and the intractable nature of the reaction mixtures prevented isolation of any pure products. *N*-Phenylmaleimide, however,



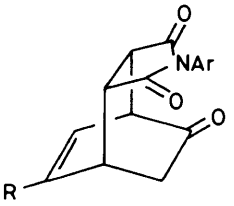
(**1**)



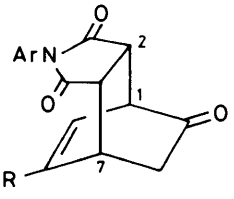
(**2**)



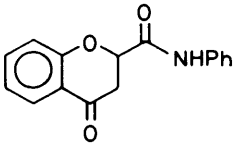
(**3**) R = OPh, Ar = Ph
(**6**) R = C_6H_4OH-*o*, Ar = Ph
(**11**) R = OC_6H_4Me-*p*, Ar = C_6H_4OMe-*p*



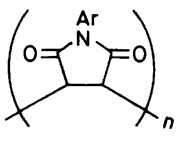
(**4**) Ar = Ph, R = H
(**10**) Ar = C_6H_4OMe-*p*, R = Me
(**12**) Ar = Ph, R = OMe



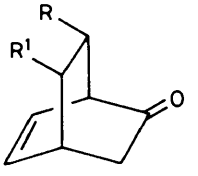
(**5**) Ar = Ph, R = H
(**9**) Ar = C_6H_4OMe-*p*, R = Me
(**13**) Ar = Ph, R = OMe



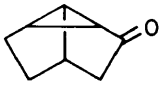
(**7**)



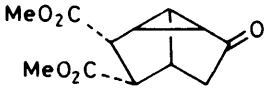
(**8**)



(**15**) R = CONHPh, R^1 = CO_2Me
or R = CO_2Me, R^1 = CONHPh
(**16**) R = R^1 = CO_2Me



(**14**)



(**17**)

proved to be a much more effective dienophile in the formation of bicyclo[2.2.2]octenones from phenols, and offered scope for varying the electrophilicity of the ethene moiety by incorporating substituents into the *N*-phenyl group.

Analysis by t.l.c. of the mixture formed on heating phenol and *N*-phenylmaleimide in a respective 2:1 molar ratio in the absence of solvent at 160—170 °C under nitrogen for 84 h revealed the presence of three products: large amounts of an insoluble polymer were also formed. The products were isolated by flash chromatography and all were found to be 1:1 adducts (M^+ = 267 m.u.) of the starting materials. The least polar adduct (**3**) (m.p. 205—207 °C) was assigned as the product of acyclic addition on the basis of its spectral properties. In particular the ^{1}H n.m.r. spectrum showed the presence of five aryl protons and a typical ABX system for the three protons of the succinimide residue.

The other two 1:1 adducts had closely similar low resolution ^{1}H n.m.r. spectra but their melting points differed and there were significant i.r. and mass spectral differences. The *exo* structure (**4**) was assigned to the less polar of these two 1:1 adducts (m.p. 243—244 °C) (and the one more difficult to obtain in a pure state) on the basis of its 220 MHz ^{1}H n.m.r. spectrum. In particular, the two hydrogens of the methylene group are affected differently by the imide carbonyl group and appear as two double doublets (J_{gem} 19 Hz) at δ2.12 (1 H, J_{vic} 2 Hz) and 2.28 (1 H, J_{vic} 3 Hz). Similar considerations allowed the assignment of the *endo* structure (**5**) to the third 1:1 adduct (m.p. 185—187 °C). Thus the chemical shift of the imide protons (2- and 6-H) are differentially affected by the C-10 carbonyl group and appear as two double doublets at δ3.42 (1 H, $J_{2,6}$8.5, $J_{1,2}$3.0 Hz) and δ3.33 (1 H, $J_{6,7}$3.0 Hz). The stereochemical assignment was confirmed by *X*-ray crystallography. The crystals are monoclinic, space group $P2_1/n$ with cell dimensions a = 10.948(8), b = 6.693(7), c = 17.875(11) Å, β = 95.5(1)°, U = 1 303.8 Å^3, Z = 4. 2 298 Independent reflections were measured on a diffractometer of which only 722 had $I > 2\sigma(I)$ and were used in subsequent calculations. The structure was determined by direct methods and refined to R 0.11.* The structure is disordered with the carbonyl oxygen positioned either on C(10) or C(11). Both O(10) and O(11) positions were refined with equal occupancy of 0.5.

The isolated yields of (**3**), (**4**), and (**5**) were respectively 3.6, 6.8, and 29% based on the amount of *N*-phenylmaleimide consumed. Unlike some Diels–Alder reactions[11] and cycloadditions to benzene,[2] the formation of (**4**) and (**5**) was not catalysed by Lewis acids, [specifically aluminium chloride, zinc chloride, palladium(III) chloride, copper(I) chloride, silver trifluoroacetate, rhenium(III) chloride, phoshoric acid or H^+ ion exchange resin IR120], but the Friedel-Crafts products (**6**) and (**7**) were formed in the presence of aluminium chloride.

In principle, compounds (**4**) and (**5**) could arise from either cycloaddition of the maleimide to the benzene ring or to the keto tautomer of phenol. 'Reverse-demand' dienophiles such as 2,3-dihydropyran and the enamine *N*-(2-methylprop-1-enyl)-morpholine may have been expected to undergo the present reaction if the keto tautomer was the intermediate, but they failed to react. Little mechanistic significance can be attached to this since acrylonitrile, methacrylonitrile, fumaronitrile, dimethyl maleate, and *p*-benzoquinone as well as the powerful dienophiles, tetracyanoethylene and *N*-phenyltriazoline-2,5-dione, all failed to react with phenol. With the exception of maleic anhydride, the only ethylenes we have observed to undergo the present reactions are maleimides and *N*-(2,6-dimethylphenyl)-maleimide proved by far the most suitable addend. Our results with a variety of maleimides are summarised in Table 1.

Table 1.

Maleimide *N*-substituent	Reactions of maleimides with phenol: Yields of cycloadducts (%)[a]	Polymer Yield[b]
H	Trace	>95
$Me(CH_2)_3$	26	30
Ph	36	33
p-MeC_6H_4	19[c]	30
p-ClC_6H_4	37	17
p-FC_6H_4	18[c]	25
p-$MeOC_6H_4$	31	11
p-$MeCOC_6H_4$	Trace	83
2,6-$(Me_2)_2C_6H_3$	63	Nil
p-$NO_2C_6H_4$	Trace	*d*
p-CNC_6H_4	Trace	*d*
1-$C_{10}H_7$	9	39

[a] Based on *N*-arylmaleimide consumed. [b] Based on *N*-arylmaleimide used. [c] Poor recovery of product from chromatography. [d] Essentially complete conversion of the imide.

As evident from Table 1, a major by-product of the cycloaddition reaction between maleimides and phenol is a polymer, the formation of which, relative to the cycloadducts, increases rapidly at temperatures greater than 170 °C. The polymer is not formed in the absence of phenol but elemental analysis showed it to be a homopolymer of the *N*-arylmaleimide. The ^{1}H n.m.r. spectrum of the polymer had no absorptions due to ethylenic protons and the i.r. spectrum had $\nu_{max.}$ at 1 715 cm^{-1} consistent with C=O stretch in *N*-substituted succinimides. Thus it is deduced that the homopolymer has units of type (**8**) rather than of the polyamide type ⟊COCH=CH–CON(Ar)⟊. The polymers are also of different type from the structurally complex polymers formed by maleic anhydride in the presence of catalysts such as triphenylphosphine.[12] It is well documented that *N*-phenylmaleimide is subject to radical polymerisation,[13] but efforts to prevent or reduce the polymerisation, under the present conditions by performing the reaction in the dark, under nitrogen, or by the use of radical traps such as diphenylamine or 2,2-diphenyl-1-picrylhydrazyl proved wholly unsuccessful. However, treatment of *N*-phenylmaleimide with weak bases such as piperidine or pyridine readily gave a polymer which had spectroscopic properties identical with those of the polymer formed by the imide in the presence of phenol. It is thus suggested that the negative moiety of a charge-transfer complex between the imide and phenol may be initiating an essentially base-catalysed polymerisation of the free and/or complex maleimide. Alternatively, the process may represent a type of zwitterionic polymerisation.

Mixing solutions of *N*-phenylmaleimide and phenol in acetonitrile produces an intensification of the yellow colour of the maleimide through increased tailing into the visible region; this is suggestive of charge-transfer complexation, even though no new absorption maximum is observed. It is, however, noteworthy from the data given in Table 1 that for *N*-arylmaleimides bearing electron-withdrawing substituents at the *p*-position (strong dienophiles), the cycloaddition reaction is either markedly (*p*-MeCO) or totally (*p*-CN and *p*-NO_2) inhibited whereas electron donor substituents (*p*-Me and *p*-MeO) increase the efficiency of the reaction and polymer formation is decreased. Thus although complexation may aid cycloaddition, those complexes in which there is a substantial charge-transfer contribution either virtually fail to add to

* Atomic co-ordinates are available from the Cambridge Crystallographic Data Centre. See Instructions for Authors (1987), para. 5.6.3 *J. Chem. Soc., Perkin Trans. 1*, 1987, Issue 1.

phenol or preferentially initiate polymerisation. The much reduced polymer formation in the case of *N*-(*p*-methoxyphenyl)-maleimide is consistent with charge-transfer catalysis of the polymerisation.

p-Cresol and *p*-methoxyphenol both gave the expected cycloaddition products with *N*-phenylmaleimide in slightly higher yields than phenol itself. *p*-Cresol formed the two stereoisomeric cycloadducts (**9**) and (**10**) with *N*-(*p*-methoxyphenyl)maleimide in respective yields of 43.5 and 18%, based on the maleimide consumed together with the product of acyclic addition (**11**) (7%), analogous to (**3**) and the maleimide polymer (20%). It is interesting to note that the adducts (**12**) and (**13**) isolated from *p*-methoxyphenol both retained the methoxy group, whereas the corresponding reaction with maleic anhydride is reported to give the demethylated ketone (**2**).[7] We were, however, unable to form an adduct from *N*-phenylmaleimide and 2,5-dimethylphenol. In this system, no intensification of the yellow colour of the imide was appparent on adding the phenol and no significant amounts of polymer were produced at 160 °C. These observations suggest that both the cycloaddition and polymerisation require precursor charge-transfer complexes and the formation of these intermediates is sensitive to steric factors.

The present facile one-step entry into bicyclo[2.2.2]octenone systems may have practical value for the synthesis of derivatives not readily accessible by other procedures. The key step in the elaboration of bicyclo[2.2.2]octenones for the enantiospecific total synthesis of cyclopentanoid natural products involves a photochemical oxa-di-π-methane rearrangement of the enone to yield the tricyclo[3.3.0.0^{2,8}]octan-3-one system (**14**).[1] In view of the importance and utility of this reaction, we have examined the photochemistry of the bicyclo[2.2.2]octenones obtained from the thermal addition of phenol and *N*-phenylmaleimide.

Direct or sensitised irradiation of either the adduct (**5**) or the amido esters (**15**) induced neither an oxa-di-π-methane reaction nor a 1,3-acyl shift process. The lack of photochemical reaction of these systems is explained by preferential excitation of the CO(NR)Ph unit in each case rather than the βγ-unsaturated ketone. The imide (**5**) by treatment with aqueous barium hydroxide followed by refluxing the product in acidified methanol, was converted into the diester (**16**) in a 60% yield after flash chromatography and distillation. Irradiation (254 nm) of (**16**) in acetone solution gave complete conversion to the required isomer (**17**) which was isolated in 75% yield following flash chromatography and recrystallisation.

The phenol maleimide cycloaddition reaction therefore offers a convenient and potentially versatile route from readily available starting materials to bicyclo- and tricyclo-octane derivatives of established synthetic utility: it is hoped that the present report will encourage further studies into the synthetic elaboration of these now readily accessible systems.

Experimental

Flash chromatography[14] was carried out with Silica Woelm 32—63 and t.l.c. with Camlab Polygram G/U.V. pre-coated sheets. Analytical g.l.c. was performed on a Hewlett Packard 5790 fitted with a flame ionisation detector and a 12.5 m phase bonded OV1 equivalent.

Mass spectra were obtained using a V.G.Micromass 70-70 spectrometer (P.C.M.U., Harwell). ^{1}H N.m.r. spectra were obtained using Varian T-60 or Perkin-Elmer R-32 spectrometers.

Synthesis of the Maleimides.—*N*-Phenylmaleimide and its derivatives were prepared from maleic anhydride and the appropriate ring-substituted aniline according to the method described by Cava *et al.*[15] *N*-Butylmaleimide was prepared in a similar manner using butylamine.

Reaction of Phenol with the Maleimides.—The reactions of the maleimides with phenol were all carried out, analysed, and worked up in the same manner. Details of the method are given here for the reaction of *N*-phenylmaleimide with phenol. The spectral data obtained for the acyclic addition products and the *exo* and *endo* cycloadducts were essentially the same as those given here for (**3**), (**4**), and (**5**) respectively. As expected, the ^{1}H n.m.r. spectra of the adducts from other maleimides differed from those of (**3**), (**4**), and (**5**) only in the resonances of the aryl protons. Analytical data and the melting points of the adducts of *N*-arylmaleimides and phenol are given in Table 2.

A mixture of phenol (10 g, 106 mmol) and *N*-phenylmaleimide (11 g, 64 mmol) was heated without solvent at 165—170 °C under nitrogen for 3 days. The orange liquid product while still warm was treated with ether (200 ml), and the resulting cream precipitate collected without undue delay. Continuous extrac-

Table 2. Analytical data for adducts of *N*-arylmaleimides with phenol

N-Arylmaleimide	Adduct	M.p. (°C), solvent	Analysis (%) C	H	N
N-(*p*-Chlorophenyl)maleimide	Acyclic adduct	237—239, $CHCl_3$	63.5	3.8	4.7
	exo-cycloadduct	282—284, EtOAc	63.6	4.1	4.6
	endo-cycloadduct	244—246, EtOAc	63.6	4.1	4.6
	($C_{16}H_{12}ClNO_3$)		(63.7)	(4.0)	(4.6)
N-(*p*-Tolyl)maleimide	Acyclic adduct	196, EtOAc	73.1	5.3	5.0
	exo-cycloadduct	257 (sub.), EtOAc	72.6	5.3	5.0
	endo-cycloadduct	242—244, EtOAc	72.9	5.3	5.0
	($C_{17}H_{15}NO_3$)		(72.6)	(5.3)	(5.0)
N-(2,6-Dimethylphenyl)maleimide	*endo*-cycloadduct	229—231, EtOAc	73.5	5.8	4.7
	($C_{18}H_{17}NO_3$)		(73.2)	(5.8)	(4.7)
N-(*p*-Fluorophenyl)maleimide	Acyclic adduct	234, $CHCl_3$	66.9	4.3	4.9
	exo-cycloadduct	259—261, MeOH	66.9	4.2	4.8
	endo-cycloadduct	198—200, MeOH	67.2	3.8	4.9
	($C_{16}H_{12}FNO_3$)		(67.3)	(4.2)	(4.9)
N-(*p*-Methoxyphenyl)maleimide	Acyclic adduct	205—208, EtOAc	67.5	5.1	4.4
	exo-cycloadduct	242—247, EtOAc	68.7	5.3	4.8
	endo-cycloadduct	204—206, EtOAc	68.8	4.9	4.8
	($C_{17}H_{15}NO_4$)		(68.7)	(5.1)	(4.7)

tion of the precipitate with ether for 8 h left an insoluble residue of colourless polymer (3.5 g, 33%).

The combined ether filtrate and extract were concentrated to 150 ml, and the solid which crystallised out overnight was filtered off. The filtrate was flash-chromatographed using chloroform–ethyl acetate (3:1) as eluant to recover starting materials (see Table 1 for cycloadduct yields based on the maleimide consumed). The subsequent product fractions were combined with the solid and re-chromatographed using the same solvent system. Early fractions contained the acyclic addition product (**3**), followed by fractions of mixed *exo*- and *endo*-cycloadduct isomers; later fractions consisted of pure *endo*-cycloadduct (**5**). Further flash chromatography of the mixed isomer fractions separated the *exo*- and *endo*-cycloadducts.

The acyclic adduct was recrystallised from acetone to give 1-*phenyl*-3-*phenoxypyrrolidine*-2,5-*dione* (**3**) as small colourless needles (300 mg, 1.8%), m.p. 205—207 °C (M^+, calc. for $C_{16}H_{13}NO_3$ 267.0895, found *m/z* 267.0896); $\nu_{max.}$(Nujol) 1 720 cm^{-1} (imide); δ_H (220 MHz; C_5D_5N) 7.68—7.10 (10 H, br m, Ph), 5.82 (1 H, dd, 3-H), 3.72 (1 H, dd, 4-H), and 3.25 (1 H, dd, 4′-H); $J_{3,4}$ 9 Hz, $J_{3,4'}$ 5 Hz, and $J_{4,4'}$ 17 Hz.

The *exo*-cycloadduct was recrystallised from ethanol to give rod-shaped colourless crystals of exo-4-*phenyl*-4-*azatricyclo*-[5.2.2.0^{2,6}]*undec*-8-*ene*-3,5,10-*trione* (**4**) (0.52 g, 3.1%), m.p. 243—244 °C (Found: C, 71.72; H, 4.55; N, 5.25. $C_{16}H_{13}NO_3$ requires C, 71.90; H, 4.87; N, 5.24%); *m/z* 267 (M^+, 100%) and 225 ($M^+ - 42$, 45%); $\nu_{max.}$(Nujol) 1 725 (ketone) and 1 715 cm^{-1} (imide); δ_H (220 MHz; $CDCl_3$) 7.24—7.58 (5 H, br m, Ph), 6.78 (1 H, dd, 8-H), 6.52 (1 H, dd, 9-H), 3.80 (1 H, dd, 1-H), 3.66 (1 H, m, 7-H), 3.28 (2 H, m, 2-H and 6-H), 2.12 (1 H, dd, 11-H), and 2.28 (1 H, dd, 11′-H); $J_{8,9}$ 6.5, $J_{8,1}$ 7.0, $J_{9,2}$ 6.5, $J_{2,6}$ 8.5, $J_{1,2}$ 3.5, $J_{1,11}$ 2.0, $J_{1,11'}$ 3.0, and $J_{11,11'}$ 19 Hz.

The *endo* cycloadduct was recrystallised from ethyl acetate to give endo-4-*phenyl*-4-*azatricyclo*[5.2.2.0^{2,6}]*undec*-8-*ene*-3,5,10-*trione* (**5**) as colourless needles (2.63 g, 14.5%), m.p. 187—188.5 °C (Found: C, 71.85; H, 4.75; N, 5.2. $C_{16}H_{13}NO_3$ requires C, 71.90; H, 4.87; N, 5.24%); *m/z* 267 (M^+, 100%), 225 ($M^+ - 42$, 85%), and 119 (78); $\nu_{max.}$(Nujol) 1 740 (ketone) and 1 710 cm^{-1} (imide); δ_H (220 MHz; $CDCl_3$) 7.25—7.60 (5 H, br m, Ph) 6.63 (1 H, dd, 8-H), 6.39 (1 H, dd, 9-H), 3.84 (1 H, dd, 1-H), 3.74 (1 H, m, 7-H), 3.42 (1 H, dd, 2-H), 3.33 (1 H, dd, 6-H), and 2.26 (2 H, s, CH_2); $J_{8,9}$ 6.5, $J_{8,1}$ 7.0, $J_{9,7}$ 6.5, $J_{2,6}$ 8.5, $J_{1,2}$ 3.0, and $J_{6,7}$ 3.0 Hz.

The same experimental procedures were also followed for the reactions of *N*-phenylmaleimide with *p*-cresol and *p*-methoxyphenol but the conditions employed for the *p*-cresol–*N*-(*p*-methoxyphenyl)maleimide system differed slightly from those given above and are, therefore, described below.

Reaction of p-*Cresol with* N-(p-*Methoxyphenyl*)*maleimide*.—*p*-Cresol (10.34 g, 0.096 mol) and *N*-(*p*-methoxyphenyl)-maleimide (11.51 g, 0.057 mol) were heated together without solvent at 170 °C for 59 h under nitrogen. The resulting dark red–brown liquid was treated while hot with ethyl acetate (250 ml) to produce a precipitate of grey–black polymer (1.70 g, 15%).

Flash chromatography of the filtrate using chloroform–ethyl acetate (3:1) resulted in facile separation of starting materials and of product isomers. After the preliminary fractions containing the starting materials, the acyclic addition product was obtained, and was recrystallised from chloroform–ethyl acetate to give 1-(p-*methoxyphenyl*)-3-(p-*methylphenoxy*)*pyrrolidine*-2,5-*dione* (**11**) as small colourless needles (950 mg, 5%), m.p. 201—202 °C (Found: C, 69.15; H, 5.3; N, 4.75. $C_{18}H_{17}NO_4$ requires C, 69.4; H, 5.5; N, 4.5%); *m/z* 311 (M^+, 100%), 203 ($M^+ - 108$, 70%), 149 (65), 134 (63), 108 (54), and 107 (57); $\nu_{max.}$(Nujol) 1 720 cm^{-1} (imide); δ_H (60 MHz; $CDCl_3$) 6.7—7.33 (8 H, br m, Ar), 5.13 (1 H, dd, 3-H), 3.80 (3 H, s, OMe), 2.97—3.57 (2 H, m, CH_2), and 2.30 (3 H, s, CMe).

The second adduct fraction was recrystallised from ethyl acetate to give colourless prisms of exo-4-(p-*methoxyphenyl*)-8-*methyl*-4-*azatricyclo*[5.2.2.0^{2,6}]*undec*-8-*ene*-3,5,10-*trione* (**10**) (2.4 g, 13%), m.p. 194—194.5 °C (Found: C, 69.25; H, 5.48; N, 4.48. $C_{18}H_{17}NO_4$ requires C, 69.44; H, 5.50; N, 4.50%); *m/z* 311 (M^+, 100%), 269 ($M^+ - 42$, 70%), 149 (62), and 134 (50); $\nu_{max.}$(Nujol) 1 730 (ketone) and 1 710 cm^{-1} (imide); δ_H (220 MHz; $CDCl_3$) 6.96—7.18 (4 H, dd, Ar), 6.01 (1 H, br d, 9-H), 3.82 (3 H, s, OMe), 3.63 (1 H, dd, 1-H), 3.32 (1 H, br m, 7-H), 3.21 (2 H, m, 2-H and 6-H), 2.15 (2 H, overlapping doublets, 11-H, 11′-H), and 1.96 (3 H, d, 8-Me); $J_{1,9}$ 6.0, $J_{1,2}$ 3.0, $J_{11,11'}$ 20, $J_{7,11}$ 2.0, $J_{7,11'}$ 3.0, and $J_{8,9}$ 20 Hz.

The final product to be eluted was the *endo* cycloadduct which was recrystallised from methanol and then from ethyl acetate to give endo-4-(p-*methoxyphenyl*)-8-*methyl*-4-*azatricyclo*[5.2.2.0^{2,6}]*undec*-8-*ene*-3,5,10-*trione* (**9**) as colourless needles (5.6 g, 31%), m.p. 188—189 °C (Found: C, 69.35; H, 5.7; N, 4.45); *m/z* 311 (M^+, 18%), 269 ($M^+ - 42$, 15%), 149 (35), 88 (65), 85 (98), and 83 (100); $\nu_{max.}$(Nujol) 1 720 (ketone) and 1 710 cm^{-1} (imide); δ_H (220 MHz; $CDCl_3$), 7.0—7.17 (4 H, dd, Ar), 5.91 (1 H, br d, 9-H), 3.85 (3 H, s, OMe), 3.69 (1 H, dd, 1-H), 3.44 (1 H, m, 7-H), 3.31 (2 H, overlapping doublets, 2-H and 6-H), 2.22 (2 H, dd, 11-H, 11′-H), and 1.92 (3 H, d, 8-Me); $J_{1,9}$ 6.0, $J_{2,6}$ 8.0, $J_{1,2}$ 3.0, $J_{6,7}$ 3.0, $J_{11,11'}$ 20 and $J_{3,9}$ 1.5 Hz.

Conversion of (**5**) *into* cis-*endo*-7,8-*Bismethoxycarbonylbicyclo*[2.2.2]*oct*-2-*en*-5-*one* (**16**).—*endo*-4-Phenyl-4-azatricyclo-[5.2.2.0^{2,6}]undec-8-ene-3,5,10-trione (**5**) (0.87 g, 3.26 mmol) was refluxed with water (65 ml) and barium hydroxide octahydrate (2.27 g, 7.2 mmol) for 5.5 h. The reaction mixture was acidified dropwise with concentrated hydrochloric acid, saturated with sodium chloride, and extracted with ethyl acetate (3 × 40 ml). The combined extracts were dried and evaporated to leave a frothy glassy solid, which was refluxed with dry methanol (50 ml) and concentrated sulphuric acid (3.5 ml) for 6 h. The mixture was concentrated to 15 ml, diluted with water (40 ml), and solid sodium hydrogen carbonate added until *just* neutral (excess base leads to liberation of free aniline). The product was extracted with ethyl acetate (4 × 30 ml), the combined extracts evaporated, and the residue flash chromatographed using diethyl ether–light petroleum (b.p. 40—60 °C) (3:2). Short-path distillation of the product afforded cis-endo-7,8-*Bismethoxycarbonylbicyclo*[2.2.2]*oct*-2-*en*-5-*one* (**16**) as a colourless oil (460 mg, 60%), b.p. 160 °C/4 mmHg (Found: M^+, *m/z* 238.0839. Calc. for $C_{12}H_{14}O_5$: *M*, 238.0842), $\nu_{max.}$(neat) 1 740 (ketone) and 1 725 cm^{-1} (ester); *m/z* 238 (M^+, 2%), 207 (6), 187 (16), 137 (100), 136 (11), 105 (38), and 91 (34); δ_H (220 MHz; $CDCl_3$) 6.48 (1 H, dd, $J_{2,3}$ 7 Hz and $J_{3,4}$ 3.5 Hz, 3-H), 6.32 (1 H, dd, $J_{2,3}$ 7 Hz and $J_{1,2}$ 3.5 Hz, 2-H), 3.73 (3 H, s, Me), 3.72 (3 H, s, Me), 3.48 (2 H, m, 1-H, 4-H), 3.36 (1 H, m, $J_{7,8}$ 6 Hz, 8-H), 3.26 (1 H, m, 7-H) and 2.18 (2 H, m, 6-H, 6′-H).

Ultraviolet Irradiation of cis-endo-7,8-*Bismethoxycarbonyl-bicyclo*[2.2.2]*oct*-2-*en*-5-*one* (**16**).—A solution of *cis-endo*-7,8-bismethoxycarbonylbicyclo[2.2.2]oct-2-en-5-one (**16**) (240 mg) in dry degassed acetone (23 ml) was irradiated in quartz at 254 nm. The reaction progress was followed by g.l.c. and was complete after 22 h. Evaporation of the acetone left an orange oil (230 mg) which was flash chromatographed using diethyl ether–light petroleum spirit (b.p. 40—60 °C) (5:4). Later fractions gave a yellow solid which was recrystallised at low temperature from diethyl ether to give cis-endo-6,7-*bismethoxycarbonyltricyclo*[3.3.0.0^{2,8}]*octan*-3-*one* (**17**) as colourless needles (180 mg, 75%), m.p. 65 °C; (Found: M^+, *m/z* 238.0844. Calc. for $C_{12}H_{14}O_5$: *M*, 238.0842) *m/z* 238 (M^+, 11%), 178 (29), 150 (24), 137 (100), 136 (31), 119 (29), and 105 (65); δ_H (220

MHz; $CDCl_3$) 3.93 (1 H, d, $J_{7,8}$ 8 Hz, 7-H), 3.76 (3 H, s, Me), 3.69 (3 H, s, Me), 3.35 (1 H, dd, 5-H), 3.30 (1 H, s, 6-H), 2.93 (1 H, dd, 1-H), 2.59 (1 H, dd, $J_{4,4'}$ 18 Hz, 4-H), 2.39 (1 H, br q, 8-H), 2.14 (1 H, d, 4'-H), and 2.00 (1 H, dd, 2-H). $J_{1,5}$ 5.0, $J_{4,5}$ 10, $J_{2,8}$ 10, $J_{1,2}$ 5.0, $J_{6,7}$ 1.0 and $J_{7,8}$ 8.0 Hz.

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