Application of 3-Oxabicyclo[3.2.0]hept-6-ene-2,4-dione (Cyclobut-3-ene-1,2-dicarboxylic Anhydride) as an Acetylene Equivalent in Cycloadditions

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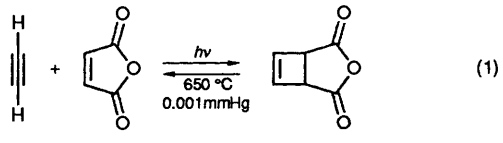
The effectiveness and limitations of dioxo-3-oxabicyclo[3.2.0]hept-6-ene-2,4-dione (cyclobut-3-ene-1,2-dicarboxylic anhydride) as an acetylene equivalent in both 1,3-dipolar and Diels–Alder cycloadditions is reported; it reacted readily with a variety of reagents, including *N*-benzylideneaniline *N*-oxide, nitrile oxides, diazomethane, cyclopentadiene, tetracyclone, anthracene, 1,2,5-triphenylphosphole 1-oxide and 1,3-diphenylisobenzofuran. The structures and stereochemistry of the adducts were deduced from their NMR data; in all cases, the sterically favoured *anti*-isomers are formed exclusively. The configuration of the Diels–Alder adducts are assigned as *endo* with the exception of that from tetracyclone (and possibly 1,3-diphenylisobenzofuran) for which an *exo*-structure is assumed on the basis of steric arguments. Adducts were not obtained with several other reagents; possible reasons for this lack of reactivity are discussed. When subjected to flash vacuum pyrolysis, the adducts underwent thermal fragmentation, either by a retro-cleavage, or by loss of maleic anhydride to form products that are derived formally from reaction of acetylene in the cycloaddition step. A concerted pathway is proposed for the pyrolytic conversion into the 'formal acetylene cycloadduct' rather than a stepwise radical mechanism.

Numerous examples of the synthesis and reactions of cyclobutenes fused to heterocyclic ring systems have been reported in the literature,[1] but so far 3-oxabicyclo[3.2.0]hept-6-ene-2,4-dione (cyclobut-3-ene-1,2-dicarboxylic anhydride) **1** has received scant attention other than as a precursor to 1,4-disubstituted dienes in ring-opening reactions.[2] Based on an observation in these laboratories[3] that the ready formation of **1** from the photochemical reaction of maleic anhydride and acetylene[4] is thermally reversible, especially under flash vacuum pyrolysis conditions[5] [eqn. (1)], we report here an investigation



(1)

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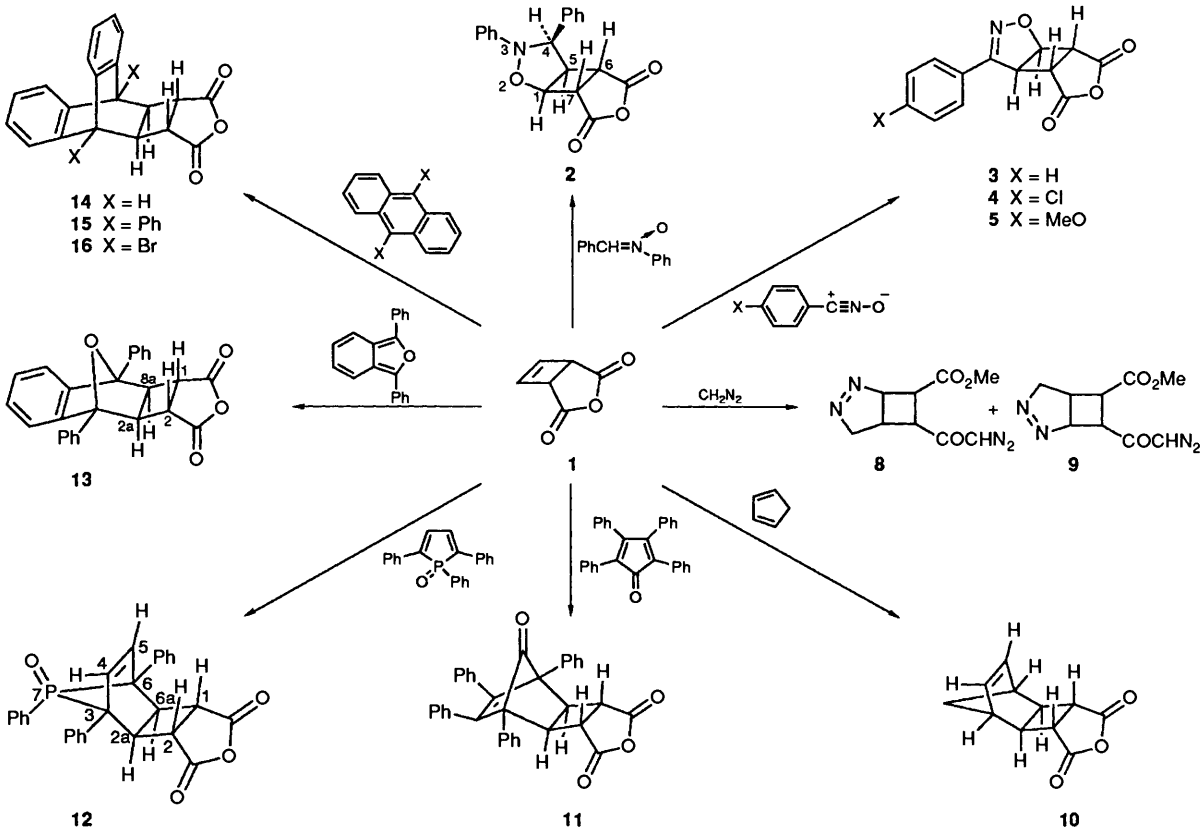
into its potential as an acetylene equivalent in cycloadditions. This type of reagent has aroused considerable recent interest[6] since acetylene itself is practically inert in such reactions except under drastic conditions of elevated temperature and pressure. Our strategy depended on the ability of **1** to give products derived from ($\pi^2 + \pi^4$)-cycloadditions which would fragment with loss of maleic anhydride when subjected to flash pyrolysis. The literature contains virtually no information concerning the reactivity of the strained double bond in **1**, but we were encouraged in our approach by reports that the compound formed a 1,3-dipolar adduct with the cyclic nitrone, 3,4-dihydroisoquinoline *N*-oxide,[7] and also underwent a Diels–Alder reaction with butadiene.[8] From a practical point of view, it would have been preferable to use the corresponding dimethyl ester of **1** as the reactant, but as it turned out, this was frustrated in many cases by its rapid thermal isomerisation[9] to (*Z*),(*E*)-dimethyl hexa-2,4-dienedioate under the forcing reaction conditions.

Results and Discussion

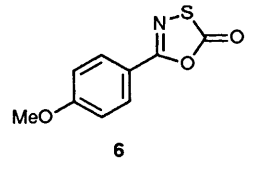
Reaction of **1** *with* 1,3-*Dipoles*.—The reactivity of **1** varied markedly over the range of 1,3-dipolar reagents studied. When **1** was heated with *N*-benzylideneaniline *N*-oxide in boiling benzene, a clean cycloaddition occurred to give the adduct **2** in 90% yield (Scheme 1). With benzonitrile oxide and its *p*-chloroanalogue, a similar reaction occurred at room temperature to give the adducts **3** and **4** in 58 and 85% yields, respectively. In the case of *p*-methoxybenzonitrile oxide, the derived adduct **5** underwent partial hydrolysis during work-up. As a result, the mixture of anhydride and diacid was esterified by acid catalysis in methanol to give the corresponding dimethyl ester, albeit in the relatively low yield of 30%. By comparison, no adduct was formed with *p*-nitrobenzonitrile oxide even when the reactants were heated in boiling toluene, or with *p*-methoxybenzonitrile sulphide, which was generated in the presence of **1** by thermolysis of a large excess of the oxathiazolone **6** in boiling xylene. Propionitrile oxide also failed to add to **1**, as did several other 1,3-dipoles, including diphenylnitrilimine, irrespective of whether it was generated by thermal or homogeneous base-induced elimination of HCl from *N*-phenylbenzohydrazonoyl chloride. The azomethine imine **7**, too, isomerised to a benzotriazole 1-oxide derivative[10] rather than react with **1**, even though this type of dipole is amongst the most active and usually takes part in cycloadditions with almost all types of multiple bonds.[11] A much lower yield (25%) than expected has been found[12] for the cycloadduct from the reaction of **7** with (*Z*)-3,4-dichlorocyclobutene for the same reason.

Cycloaddition also failed to take place with ethyl azidoformate even under photolytic conditions. Nor could adducts be obtained with 2-hydroxyphenyl azide, 2-tosyloxyphenyl azide and α-azidophenylacetic acid. An adduct was isolated from the reaction of **1** with diazomethane, but from its analysis, mass spectrum and other spectroscopic evidence this was adjudged to be a 1:1 mixture of **8** and **9** in which the anhydride function had been cleaved to form a diazoketone.[13]

The inertness of compound **1** to many of the preceding 1,3-dipoles points to the fact that the double bond is relatively electron deficient. This deficiency is reflected to some degree by the ionisation potential (πI_p) of **1** which was found by us to be substantially higher (10.49 eV)[14] than that of comparison olefins, *e.g.* cyclobutene (πI_p = 9.43 eV). We explained this



Scheme 1



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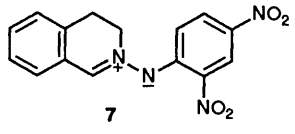

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difference in terms of a net mixing (through bond and through space) of the carbonyl molecular orbital with the π-molecular orbital. As a result there is a lowering of the energy of the latter orbital. According to perturbation molecular orbital theory, for a dipole-HOMO-controlled process,[15] as might be expected here, only those 1,3-dipoles with a relatively high energy HOMO should react most readily with **1**. Houk *et al.*[16] give the HOMO energies for many of the 1,3-dipoles used in this study and the values are in good agreement with the observed reactivity apart from the azomethine imine **7** ($E_{HOMO} = -5.6$ eV) which does not react with **1** owing to a more competitive isomerisation to a benzotriazole 1-oxide derivative (*vide supra*).

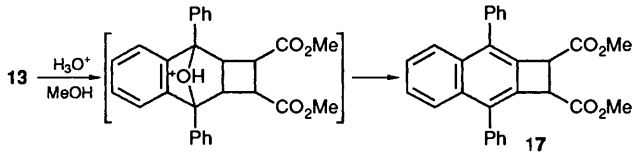
Reaction of **1** *with* 1,3-*Dienes*.—Diels–Alder adducts could not be obtained from **1** with an excess of furan (sealed tube; 80 °C) or with 2,5-dimethylfuran, 3,6-di(2-pyridyl)-1,2,4,5-tetrazine, and tetrachloro-*o*-benzoquinone in boiling benzene, even in the presence of Lewis acid catalysts. Conversely, addition to cyclopentadiene occurred readily in boiling benzene to give the adduct **10** in almost quantitative yield. Good yields of the adducts **11**, **12** and **13** were also isolated from the corresponding reactions with 2,3,4,5-tetraphenylcyclopentadienone(tetracyclone), 1,2,5-triphenylphosphole 1-oxide and 1,3-diphenylisobenzofuran, respectively in boiling benzene. No reaction occurred between **1** and anthracene, 9,10-diphenylanthracene or 9,10-dibromoanthracene under the former conditions, whereas in boiling xylene it formed the cycloadducts **14**, **15** and **16** in moderate-to-good yields as stable crystalline compounds.

Structures and Stereochemistry of Cycloaddition Products.—The structures of the adducts were supported by their complementary spectral data. ^{1}H NMR analysis of the adducts showed that cycloaddition with **1** was highly stereospecific in all cases, giving the sterically favoured *anti*-isomers as the sole isolated products (TLC analysis of the crude reaction mixtures showed little if any trace of *syn*-adducts). This assignment followed from the coupling constants for the cyclobutane ring protons which were those expected for an *anti*-configuration.[17] For example, the 1,3-dipolar adduct **5**; X = OMe showed both a low J value (3.0 Hz), indicative of a *trans* vicinal relationship, and a high J value (8.0 Hz) for a *cis*-interaction of adjacent protons. The corresponding *cis*- and *trans*-couplings for adduct **2** were 5.5 and 2.0 Hz, respectively. We assume that **2** is formed by *exo*-addition of the *Z*-isomer of *N*-benzylideneaniline *N*-oxide since there is also a *cis*-relationship between the protons at positions 4 and 5 as evidenced by the large coupling constant ($J_{4,5} = 6.5$ Hz).[7] This assignment is further supported by the chemical shift of 6-H which appears at higher field than 7-H (δ 3.05 *vs. ca.* 3.8) as a result of strong shielding by the *C*-phenyl group of the isoxazolidine moiety.

The exclusive formation of a single isomer precluded a definitive assignment of structure for the Diels–Alder adducts in every case. As a rule, secondary orbital interactions favour *endo*-addition,[18] even with non-conjugated olefins[19] unless steric factors operate when the selectivity can be reversed in favour of the *exo*-adduct. For cyclopentadienes, substituents in the 2,3-positions (and the equivalent 3,4-positions of the corresponding

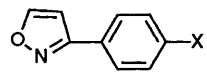
dienone) tend to increase the $\Delta G^{\ddagger}$ of the *endo*-transiton state,[20] and accordingly, in the case of tetracyclone, of the two possible orientations, the *exo*-form **11** is more likely. Likewise, the formation of a single isomer in the reaction with 1,3-diphenylisobenzofuran did not allow the attribution of a definitive structure to the adduct **13**, but generally for this reagent *endo*-adducts are less stable than the *exo*-adducts,[21] and on this basis, **13** is tentatively assigned as *exo*. On the other hand, more serious steric repulsions should prevail in the *exo*-transition state for the reaction with 1,2,5-triphenylphosphole 1-oxide owing to the presence of a 1-substituent. This is borne out by the formation of a single adduct **12** to which the *endo*-configuration is assigned by virtue of a lack of coupling between the bridgehead phosphorus and 2a-H and 6a-H because of a dihedral angle of *ca.* 90°;[22] had *exo*-addition been preferred, the dihedral angle would be close to 180° and a strong coupling would have resulted, as found for the olefinic protons where $^{3}J_{PH}$ = 10 Hz. The latter protons are strongly deshielded (7.01 ppm) which is consistent with a *syn*-arrangement of the phosphoryl oxygen as shown in **12**.

The configuration of the sole adduct **10** from the reaction with cyclopentadiene was unequivocally assigned as *endo* by spectral comparison with an authentic sample of the *exo*-isomer which was prepared according to the method of Tabushi *et al.*[23] from the (2_{δ} + 2_{δ} + 2_{π})-cycloaddition between quadricyclane and maleic anhydride. In particular, the resonance of the olefinic protons in **10** appeared at lower field (δ 6.40); for the related *exo*-adduct they absorb at δ 6.09. The *anti*-stereochemistry of **10** also followed from its ^{1}H NMR spectrum which showed a cyclobutane ring coupling constant ($J_{2,2a}$) of 1.6 Hz, much lower than the minimum value of 5 Hz arising from *cis*-interactions of adjacent protons. Addition onto the *anti*-face of **1** by cyclopentadiene contrasts with the behaviour of (*Z*)-3,4-dichlorocyclobutene[20] which undergoes a similar cycloaddition to form only the *syn-endo* isomer by virtue of favourable secondary orbital interactions. The assignment of an *anti*-configuration to each of the other cycloadducts of **1** also followed from the small coupling constants found for the cyclobutane protons, *e.g.* $J_{2,2a}$ + $J_{2,8a}$ or $J_{1,8a}$ + $J_{1,2a}$ values in **13** were 3.0 Hz as expected for a *trans*-relationship. In this particular case, the coupling disappeared when the adduct was esterified in boiling methanolic hydrogen chloride due to its concomitant aromatisation to **17**.



The reason for the overwhelming preference by **1** to form adducts with *anti*-stereochemistry is presumably steric in origin, although dipole–dipole interactions must also operate in the cycloadditions with 1,3-dipoles and favour *anti*-attack. As regards secondary orbital interactions, these are clearly insufficient to overcome the severe steric interaction of the anhydride moiety in **1** and direct attack to its *syn*-face, but where steric demands are similar as in the *exo*- and *endo*-addition of **1** to cyclopentadiene, the exclusive observation of the latter points to a well-defined attractive secondary interaction.

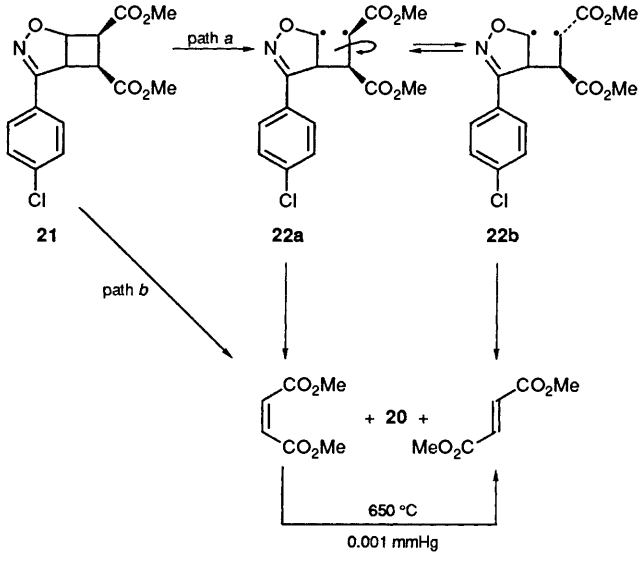
Flash Vacuum Pyrolysis (FVP) *Studies.*—Basically, two different modes of fragmentation can be discerned in the thermal fragmentation of the adducts under flash pyrolysis conditions. Either retro-cleavage resulted, or the adducts extruded maleic anhydride to form products that are 'formal acetylene cycloadducts.' For example, at 600 °C and 0.001 mmHg, the adduct **3** cleaved with the loss of maleic anhydride to give 3-phenylisoxazole **18** in 71% yield after chromatography of the crude pyrolysate. In the case of the *p*-methoxy derivative



18 X = H
19 X = MeO
20 X = Cl

5, pyrolysis of its dimethyl ester under the same conditions resulted in a similar fragmentation to yield the isoxazole **19** in 64% yield, whilst the diacid of the *p*-chloroanalogue **4** gave the isoxazole **20** in 44% yield. Heating of the carbonyl-bridged adduct **11** at its melting point led to ill-defined decomposition, but under FVP conditions at 600 °C, it underwent a smooth fragmentation to maleic anhydride, carbon monoxide and a yellow oil which was identified as 1,2,3,4-tetraphenylbenzene (72%) by spectral comparison with an authentic sample. Attempts to eliminate carbon monoxide specifically by pyrolysis at lower temperatures led to lower yields of the same product. Pyrolysis of the adduct **12** under the same conditions led to a similar loss of the bridging group (PhPO) in tandem with that of maleic anhydride. As a result, *p*-terphenyl formed in 80% yield compared with the previous highest yield of 57% which was obtained by using phenyl vinyl sulphoxide as an acetylene equivalent in a Diels–Alder cycloaddition with 1,4-diphenylbuta-1,3-diene.[24]

Reasonable mechanistic options for the cleavage of the cyclobutane ring in the foregoing pyrolyses include a concerted pathway or a stepwise radical process. We have examined the products from the pyrolysis of (*Z*)-dimethyl ester **21** and find that in addition to the isoxazole **20**, both dimethyl maleate and dimethyl fumarate are formed in the ratio of 5:1, respectively. A stepwise mechanism (path *a* in Scheme 2), whereby rotation



Scheme 2

occurs around the carbon–carbon bond in the diradical species **22**, could account for the loss of stereochemical control, but since dimethyl maleate is isomerised to fumarate to the same extent when subjected to FVP under identical conditions, it seems likely that the fragmentation proceeds in a concerted manner (path *b*).

All the other adducts underwent retro-cycloaddition at their m.p.s or when subjected to FVP. For example, at 600 °C, the

adduct **13** gave a mixture containing 1,3-diphenylisobenzofuran (98%), maleic anhydride (55%) and a small amount (<5%) of cyclobut-3-ene-1,2-dicarboxylic anhydride. In a separate pyrolysis experiment, the formation of the maleic anhydride was seen to occur by loss of acetylene from cyclobut-3-ene-1,2-dicarboxylic anhydride. In the case of adduct **14**, it was hoped to form dibenzobarralene by elimination of maleic anhydride, but at 600 °C the only products to be isolated were anthracene and cyclobut-3-ene-1,2-dicarboxylic anhydride in good yields.

In conclusion, our results show that while cyclobut-3-ene-1,2-dicarboxylic anhydride can function as an acetylene equivalent in certain reactions, it does not in others. Its utility is most apparent in cycloadditions with 1,3-dipoles, but the failure to form cycloadducts with many reagents is clearly a limitation on the synthetic versatility of the method. In contrast, many dienes are sufficiently reactive to form Diels–Alder adducts with **1** but these tend to undergo retro-cleavage on pyrolysis, unless as in the case of the tetracyclone adduct **11**, an aromatic molecule is extruded.

Experimental

Melting points are uncorrected. Unless stated otherwise, ^1H and ^{13}C NMR spectra were recorded at 100 and 20 MHz, respectively for solutions in deuteriochloroform. Coupling constants are in Hz. IR spectra were recorded for Nujol mulls. Mass spectra were recorded on an AEI MS 902 mass spectrometer at 70 eV.

Cyclobut-3-ene-1,2-dicarboxylic Anhydride **1**.—The title compound was prepared in 49% yield by the method of Bloomfield *et al.*,[25] which was an adaption of Hartmann's original procedure.[4]

Reaction of Cyclobut-3-ene-1,2-dicarboxylic Anhydride **1**.—(a) *With* N-*benzylideneaniline* N-*Oxide*.[26] A solution of cyclobut-3-ene-1,2-carboxylic anhydride (2.97 g, 24 mmol) and the nitrone (4.73 g, 24 mmol) in dry benzene (60 ml) was heated under reflux overnight. After filtration, the solution was evaporated to dryness and the colourless residue recrystallised from diethyl ether (twice) to give 3,4-*diphenyl-2-oxa-3-azabicyclo*[3.2.0]*heptane-6,7-dicarboxylic anhydride* **2** (6.89 g, 90%) as a fluffy solid, m.p. 188–193 °C decomp. (Found: C, 71.3; H, 4.7; N, 4.4. $C_{19}H_{15}NO_4$ requires C, 71.0; H, 4.7; N, 4.46%); ν_{max}/cm^{-1} 1858, 1784, 1590, 1487, 1233, 1195, 1144, 1072, 1055, 912, 895, 752 and 733; $\delta_H([^2H_6]DMSO)$ 3.06 (1 H, dd, *J* 6.9 and 2.8, 6-H), 3.62–4.0 (2 H, m, 5-H and 7-H), 4.61 (1 H, d, *J* 6.4, 4-H), 5.20 (1 H, dd, *J* 5.8 and 2.0, 1-H) and 6.98–7.45 (10 H, m, Ph); *m/z* 321 (M^+, 47%), 194 (10), 181 (8), 180 (11), 91 (100) and 77 (30).

The anhydride **2** (2.35 g, 7.3 mmol) was dissolved in 0.6 mol dm^3 aqueous sodium hydroxide (2.0 ml) and the solution boiled under reflux for 10 min. After cooling to room temperature, the solution was carefully acidified with conc. hydrochloric acid to give 3,4-*diphenyl-2-oxa-3-azabicyclo*[3.2.0]*heptane-6,7-dicarboxylic acid* (2.41 g, 97%) as colourless crystals, m.p. 175–177 °C decomp. (Found: C, 67.55; H, 5.3; N, 4.2. $C_{19}H_{17}NO_5$ requires C, 67.25; H, 5.05; N, 4.1%); ν_{max}/cm^{-1} 3400br, 2600br, 1700, 1592, 1450, 1370, 1252, 1218, 1065, 828, 758, 748, 700 and 690; $\delta_H([^2H_6]$acetone) 2.93 (1 H, dd, *J* 10.5 and 3.5), 3.68–3.91 (2 H, m), 4.55 (1 H, d, *J* 7.5), 5.16 (1 H, dd, *J* 7.0 and 4.5), 6.93–7.52 (10 H, m, Ar) and 8.02 (2 H, br s); *m/z* 339 (M^+, 1%), 321 (13), 181 (60), 180 (56), 169 (62), 91 (56) and 77 (100).

(b) *With benzonitrile oxide*.[27] Triethylamine (0.40 g, 4 mmol) in dry tetrahydrofuran (5 ml) was added dropwise to a stirred solution of cyclobut-3-ene-1,2-dicarboxylic anhydride (0.50 g, 4 mmol) and phenylhydroximoyl chloride (0.63 g, 4 mmol) in dry tetrahydrofuran (25 ml) at room temperature. After 1 h the precipitated triethylamine hydrochloride (0.55 g, 91% activation to the 1,3-dipole) was filtered off and the solvent evaporated under reduced pressure to give a pale brown oil (0.98 g). Trituration of the oil with chloroform afforded an easily hydrolysable colourless solid (0.22 g, m.p. 171–176 °C), which was identified as 4-*phenyl-2-oxa-3-azabicyclo*[3.2.0]*hept-3-ene-6,7-dicarboxylic anhydride* **3**, ν_{max}/cm^{-1} 1855 (anhydride C=O), 1780 (C=O), 1064 (anhydride C–O–C), 908 and 765; *m/z* 243 (M^+, 26%), 197 (9), 145 (78), 144 (100) and 77 (52).

The residual oil after trituration showed a strong IR absorption at 1730 cm^{-1} and exchangeable (D_2O) ^1H NMR signal at δ *ca.* 9.5. The residue was dissolved in 2% aqueous sodium hydroxide, extracted with chloroform and red-acidified to pH 2 with 6 mol dm^{-3} hydrochloric acid to give a colourless crystalline solid (0.38 g). Recrystallisation from chloroform (twice) afforded 4-*phenyl-2-oxa-3-azabicyclo*[3.2.0]*hept-3-ene-6,7-dicarboxylic acid*, m.p. 218–220 °C decomp. (Found: C, 59.65; H, 4.2; N, 5.2. $C_{15}H_{13}NO_5$ requires C, 59.8; H, 4.2; N, 5.4%); ν_{max}/cm^{-1} 1725, 1687, 1300, 1186 and 855 cm^{-1}; *m/z* 261 (M^+, 2%), 243 (11), 199 (100), 155 (78), 154 (62), 145 (40), 144 (42) and 77 (55).

(c) *With* p-*chlorobenzonitrile oxide*.[27] To a solution of cyclobut-3-ene-1,2-dicarboxylic anhydride (0.82 g, 0.0067 mol) and *p*-chlorophenylhydroximoyl chloride (1.25 g, 0.0067 mol) in dry tetrahydrofuran (55 ml) was added freshly distilled triethylamine (0.67 g, 0.0067 mol). The mixture was stirred for 3 h after which the triethylamine hydrochloride (0.81 g, 89% activation to the 1,3-dipole) which had formed was filtered off. The filtrate was evaporated to dryness, leaving a fawn-coloured solid which upon trituration with dry diethyl ether furnished a colourless solid (1.83 g, m.p. 167–176 °C). Recrystallisation from benzene gave 4-(p-*chlorophenyl*)-2-*oxa*-3-*azabicyclo*-[3.2.0]*hept*-3-*ene*-6,7-*dicarboxylic anhydride* **4** (1.57 g, 85%) which failed to analyse correctly owing to contamination by the corresponding diacid. The impure anhydride (1.0 g) was dissolved in water (10 ml) and boiled for 10 min. Cooling of the filtered aqueous solution deposited colourless crystals (m.p. 185–192 °C) of 4-(p-*chlorophenyl*)-2-*oxa*-3-*azabicyclo*[3.2.0]-*hept*-3-*ene*-6,7-*dicarboxylic acid* (0.9 g, 85%) (Found: C, 52.7; H, 3.4; N, 4.7. $C_{13}H_{13}ClNO_5$ requires, C, 52.8; H, 3.4; N, 4.7%); ν_{max}/cm^{-1} 3160br, 1715, 1195, 1088, 868 and 830; $\delta_H([^2H_6]$-acetone) 3.59 (2 H, dd), 4.38 (1 H, dd), 5.49 (1 H, dd), 7.40 (2 H, d) and 7.69 (2 H, d); *m/z* 297, 295 (M^+), 279, 277 ($M^+ - H_2O$), 235, 233 ($M^+ - H_2O$, $-CO_2$), 205, 207 ($M^+ - H_2O$, $-CO_2$, $-CO$), and 181, 179.

The diacid (200 mg, 0.68 mmol) was added to an ethereal solution of diazomethane and stirred at room temperature for several hours during which time gas evolution gradually ceased. Excess of diazomethane was destroyed by addition of dilute acetic acid and, after washing with water, 5% aqueous sodium hydrogen carbonate, and water again, the ethereal layer was dried ($MgSO_4$). Removal of ether under reduced pressure gave *dimethyl* 4-(p-*chlorophenyl*)-2-*oxa*-3-*azabicyclo*[3.2.0]*hept*-3-*ene*-6,7-*dicarboxylate* **23** as a pale-yellow oil (195 mg, 89%) which gradually crystallised on trituration with diethyl ether, m.p. 93–97 °C; ν_{max}/cm^{-1} 1737, 1242 and 1095; *m/z* 325, 323 (M^+, 26%), 266, 264 (37), 234, 232 (36), 181, 179 (100) and 113 (94).

(d) *With* p-*methoxybenzonitrile oxide*.[28] Freshly distilled triethylamine (0.440 g, 4.36 mmol) was added to a stirred solution of cyclobut-3-ene-1,2-dicarboxylic anhydride (0.541 g, 4.36 mmol) and *p*-methoxybenzohydroximoyl chloride (0.810 g, 4.36 mmol) in dry tetrahydrofuran (40 ml) at room temperature. After 3 h the colourless precipitate of triethylamine hydrochloride (0.560 g, 93% activation to the 1,3-dipole) which had formed was filtered off. The filtrate was evaporated to dryness to give the crude adduct **5** as a yellow gum (1.19 g), which failed to crystallise owing to partial hydrolysis to the corresponding diacid (δ_H 9.7). The gum was dissolved in methanol (40 ml) containing several drops of concentrated

sulphuric acid and the mixture was boiled under reflux for 3 h. The solution was allowed to cool and water (20 ml) was added. The methanol was removed by evaporation and the product was extracted from the aqueous solution with dichloromethane (4 × 15 ml). The dichloromethane extract was dried and evaporated to give a colourless solid which was recrystallised from ethanol to give *dimethyl* 4-(p-*methoxyphenyl*)-2-*oxa*-3-*azabicyclo*[3.2.0]*hept*-3-*ene*-6,7-*dicarboxylate* (386 mg, 30%) as needles, m.p. 121.5–123 °C (Found: C, 60.15; H, 5.35; N, 4.4. $C_{16}H_{17}NO_6$ requires C, 60.3; H, 5.45; N, 4.25%); ν_{max}/cm^{-1} 1730 (CO), 1610 (C=C), 1520 (C=N), 1260 (CO–O–C) and 1180 (CO–O–C); δ_H 3.63 (2 H, dd, 6-H and 7-H), 3.70 (3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 4.42 (1 H, dd, *J* 8 and 3, 5-H), 5.56 (1 H, dd, *J* 8 and 3, 1-H), 6.89 (2 H, d, *J* 7, Ar) and 7.59 (2 H, d, *J* 7, Ar); *m*/*z* 319 (M^+, 38%), 260 (11), 228 (16), 205 (9.5), 200 (8), 175 (100), 160 (8), 147 (19), 113 (16) and 113 (46).

(e) *With diazomethane.* Cyclobut-3-ene-1,2-dicarboxylic anhydride (0.35 g) was added to an ethereal solution of diazomethane prepared from diazald (4.3 g) and potassium hydroxide [0.8 g in 96% aqueous ethanol (20 ml)]. After being stirred overnight at room temperature, the reaction mixture was filtered, and the solvent evaporated to give a pale-yellow oil (0.26 g) which even after chromatography [alumina; light petroleum (40–60 °C)–chloroform] failed to crystallise. Spectroscopic examination of the oil indicated it to be a *ca.* 1:1 mixture of 3*H*-pyrazolines **8** and **9**; ν_{max}/cm^{-1} 2096, 1730, 1626 and 1365; δ_H 2.60–3.55 (3 H, m), 3.71 (3 H, s), 3.78 (3 H, s), 4.40–4.75 (2 H, m) and 5.20–5.70 (2 H, m); *m*/*z* 194 ($M^+ - N_2$, 18%), 180 (52) and 124 (100).

(f) *With cyclopentadiene.* Cyclobut-3-ene-1,2-dicarboxylic anhydride (0.37 g, 2.98 mmol) was suspended in dry benzene (30 ml). To this was added cyclopentadiene (0.246 g, 3.7 mmol, 25% w/w excess). The resulting mixture was boiled under reflux for 12 h, after which time an insoluble colourless solid (53 mg) was filtered off. This was later identified as buta-1,3-diene-1,4-dicarboxylic acid. After evaporation of the filtrate to dryness, the solid residue was vacuum sublimined at 140 °C and 0.05 mmHg to give endo-1,2,2a,3,6,6a-*hexahydro*-3,6-*methanobenzocyclobutene*-1,2-*dicarboxylic anhydride* **10** (0.528 g, 93%) as colourless crystals, m.p. 98–99 °C (Found: C, 69.3; H, 5.4. $C_{11}H_{10}O_3$ requires C, 69.5; H, 5.3%); ν_{max}/cm^{-1} 1848 (C=O) 1780 (C=O) and 1065 (C–O); δ_H 1.07–1.22 (1 H, d, *J* 9, 7-H), 1.64–1.76 (1 H, d, *J* 9, 7-H), 2.67–2.70 (2 H, m, 6a-H and 2a-H), 2.88–2.98 (2 H, m, 6-H and 3-H), 3.11–3.22 (2 H, m, 1-H and 2-H) and 6.40 (2 H, t, *J* 2, 4-H and 5-H); δ_C 41.75, 42.11, 45.02, 50.50, 136.09 and 173.26 (quat C); *m*/*z* 190 (M^+, 100%), 162 (33), 145 (28) and 131 (21).

(g) *With tetracyclone.*[29] A solution of cyclobut-3-ene-1,2-dicarboxylic anhydride (0.25 g, 2.0 mmol) and tetracyclone (0.77 g, 2.0 mmol) in anhydrous benzene (50 ml) was boiled under reflux for 18 h. The solution was evaporated to give a dark purple residue which was triturated with ice-cold diethyl ether to afford a pale purple crystalline solid. Recrystallisation from chloroform (twice) gave 7-*oxo*-3,4,5,6-*tetraphenyl*-1,2,2a,3,6,6a-*hexahydro*-3,6-*methanobenzocyclobutene*-1,2-*dicarboxylic anhydride* **11** (0.43 g, 42%) as colourless crystals, m.p. 234–235 °C (decomp.) (Found: C, 82.9; H, 4.85. $C_{35}H_{24}O_4$ requires C, 82.7; H, 4.75%); ν_{max}/cm^{-1} 1865 (C=O), 1790 (C=O), 1780 (C=O), 1600 (aromatic ring) and 1030 (anhydride C–O–C); δ_H([$^2H_6$]acetone) 3.30–3.22 (2 H, m, 6a-H and 2a-H), 4.00–3.92 (2 H, m, 1-H and 2-H), 6.90 (10 H, s, Ph) and 7.40–7.14 (10 H, m, Ph); *m*/*z* 508 (M^+, 2.6%), 480 (15), 452 (26), 383 (53) and 382 (100).

(h) *With* 1,2,5-*triphenylphosphole* 1-*oxide.*[30] A solution of cyclobut-3-ene-1,2-dicarboxylic anhydride (0.25 g, 2.0 mmol) and 1,2,5-triphenylphosphole 1-oxide (0.66 g, 2.0 mmol) in dry benzene (25 ml) was boiled under reflux for 6 h and then allowed to cool to room temperature during which time large colourless cube-shaped crystals formed in the reaction flask. The crystals were filtered off and recrystallisation from benzene–acetone, followed by chloroform, gave 7-*oxo*-3,6,7-*triphenyl*-1,2,2a,3,6,6a-*hexahydro*-3,6-*methano*-7-*phosphabenzocyclobutene*-1,2-*dicarboxylic anhydride* **12** (0.35 g, 39%) as colourless rhombs, m.p. 204–206 °C (Found: C, 74.6; H, 4.6. $C_{22}H_{21}O_4P$ requires C, 74.3; H, 4.7%); ν_{max}/cm^{-1} 1843, 1775, 1595, 1240, 1232, 1195, 1178, 1108, 1070, 1052, 927 and 915; δ_H([$^2H_6$]DMSO) 3.00–2.88 (2 H, m), 4.18–4.09 (2 H, m), 7.01 (2 H, d, J_{PH} 10) and 7.10–7.58 (15 H, m, Ar); δ_P 80.1; *m*/*z* 328 (M^+ – PhPO, 12%), 230 (100) and 115 (16).

(i) *With* 1,3-*diphenylisobenzofuran.* A solution of cyclobut-3-ene-1,2-dicarboxylic anhydride (0.47 g, 3.8 mmol) and 1,3-diphenylisobenzofuran (1.07 g, 3.9 mmol) in dry benzene (80 ml) was boiled under reflux for 4 h. During this time the yellow fluorescence of the solution was reduced considerably in intensity and TLC confirmed that most of the 1,3-diphenylisobenzofuran had reacted. The solution was evaporated under reduced pressure to afford colourless crystals and recrystallisation from chloroform–hexane (2:1) gave 3,8-diphenyl-3,8-epoxy-1,2,2a,3,8,8a-hexahydrocyclobuta[*b*]naphthalene-1,2-carboxylic anhydride **13** (1.021 g, 68%) as needles. The product was sublimed (150 °C at 0.3 mmHg) to give analytically pure colourless prisms, m.p. 268–269 °C (Found: C, 78.9; H, 4.45. $C_{26}H_{18}O_4$ requires C, 79.2; H, 4.6%); ν_{max}/cm^{-1} 1865 (anhydride C=O), 1855 (C=O), 1790 (C=O), 1196, 1075 and 910 (C–O–C); δ_H 3.11 (2 H, dd, *J* 2 and 1, 8a-H and 2a-H), 3.30 (2 H, dd, *J* 2 and 1, 1-H and 2-H), 6.80–7.04 (2 H, m, Ar), 7.04–7.26 (2 H, m, Ar) and 7.40–7.74 (10 H, m, Ph); *m*/*z* 394 (M^+, 55%), 296 (8), 270 (100), 241 (9), 165 (8), 135 (7), 105 (9) and 77 (13).

A solution of the anhydride **13** (0.62 g) in methanol (25 ml) was saturated with hydrogen chloride gas and then boiled under reflux for 4 h. Evaporation of the solvent under reduced pressure followed by recrystallisation from methanol gave *dimethyl* 3,8-*diphenyl*-1,2-*dihydrocyclobuta*[b]*naphthalene*-1,2-*dicarboxylate* **17** as colourless plates (0.48 g, 73%), m.p. 196–197.8 °C (Found: C, 79.4; H, 5.3. $C_{28}H_{22}O_4$ requires C, 79.6; H, 5.3%); ν_{max}/cm^{-1} 1748 and 1730; δ_H 3.51 (6 H, s), 4.72 (2 H, s), 7.36–7.44 (2 H, m, Ar), 7.46 (10 H, br s, Ph) and 7.87–7.96 (2 H, m, Ar); δ_C 48.46, 51.66, 125.41, 126.18, 127.44, 128.17, 129.86, 133.45, 133.83, 135.99, 136.20 and 170.01; *m*/*z* 422 (M^+, 100%), 363 ($M^+ - CO_2CH_3$, 80) and 303 (56).

(j) *With anthracene.* A mixture of cyclobut-3-ene-1,2-dicarboxylic anhydride (6.0 g, 48 mmol) and anthracene (8.6 g, 48 mmol) in dry toluene (300 ml) was boiled under reflux for 168 h. The solvent was evaporated to give a colourless solid which was purified by sublimation (150 °C, 0.2 mmHg) to give 1,2,2a,3,8,8a-*hexahydro*-3,8-(o-*benzeno*)*cyclobuta*[b]-*naphthalene*-1,2-*dicarboxylic anhydride* **14** (11.4 g, 78%) as colourless crystals, m.p. 255–256 °C (Found: C, 79.2; H, 4.55. $C_{20}H_{14}O_3$ requires C, 79.45; H, 4.65%); ν_{max}/cm^{-1} 1860 (C=O), 1230, 1060 and 910 (C–O–C); δ_H 2.52–2.60 (2 H, m, 2a-H and 8a-H), 2.88 (2 H, m, 1-H and 2-H), 4.50 (2 H, t, *J* 2, 3-H and 8-H) and 7.04–7.42 (8 H, m, Ar); *m*/*z* 302 (M^+, 58%), 229 (16), 202 (13), 178 (100), 152 (16) and 101 (26).

(k) *With* 9,10-*diphenylanthracene.* A mixture of cyclobutene-3,4-dicarboxylic anhydride (0.37 g, 3.0 mmol) and 9,10-diphenylanthracene (1.00 g, 3.0 mmol) in dry toluene (120 ml) was boiled under reflux for 69 h. The solvent was evaporated to give a pale-yellow solid whose ^{1}H NMR spectrum showed that none of the starting materials remained. Recrystallisation from diisopropyl ether gave 3,8-*diphenyl*-1,2,2a,3,8,8a-*hexahydro*-3,8-(o-*benzeno*)*cyclobuta*[b]*naphthalene*-1,2-*dicarboxylic anhydride* **15** (0.74 g, 53%) as off-white crystals, m.p. >300 °C (Found: C, 84.75; H, 5.1. $C_{32}H_{22}O_3$ requires C, 84.6; H, 4.9%); ν_{max}/cm^{-1} 1860 (C=O), 1785 (C=O), 1600 (C=C), 1230, 1065 and 930 (C–O–C); δ_H 1.68–1.80 (2 H, m, 2a-H and 8a-H), 2.42–2.56 (2

H, m, 1-H and 2-H), 6.76–7.00 (8 H, m, Ar) and 7.06–7.90 (10 H, br m, Ph); *m/z* 454 (M^+, 4%), 330 (100) and 252 (29).

(l) *With* 9,10-*dibromoanthracene*. A mixture of cyclobut-3-ene-1,2-dicarboxylic anhydride (2.0 g, 16.1 mmol) and 9,10-dibromoanthracene (5.6 g, 16.7 mmol) in dry toluene (140 ml) was boiled under reflux for 168 h. The solvent was evaporated to give a colourless solid whose ^{1}H NMR spectrum showed that very little of the starting materials remained. Recrystallisation from diisopropyl ether gave 3,8-*dibromo*-1,2,2a,3,8,8a-*hexahydro*-3,8-(o-*benzeno*)*cyclobuta*[b]*naphthalene*-1,2 *dicarboxylic anhydride* **16** (6.6 g, 86%) as colourless crystals, m.p. 185–186 °C (Found: C, 52.4; H, 2.55. $C_{20}H_{12}Br_2O_3$ requires C, 52.15; H, 2.65%); ν_{max}/cm^{-1} 1860 (C=O), 1780 (C=O), 1230, 1070 and 975 (COC); δ_H 2.58–.2.70 (2 H, m, 2a-H and 8a-H), 3.18–3.32 (2 H, m, 1-H and 2-H), 7.18–7.44 (4 H, m, Ar) and 7.68–7.84 (4 H, m, Ar); *m/z* 460 (M^+, 25%), 336 (100), 228 (27), 202 (16), 200 (13), 176 (14), 124 (23), 122 (30), 104 (15) and 102 (13).

General Procedure for Pyrolyses.—A sample was volatilised from a tube in a Büchi Kugelrohr oven, through a 30 × 2.5 cm silica tube. This was heated at temperatures in the range 350–900 °C by a Stanton Redcroft laboratory tube furnace LM8100, the temperature being measured by a Pt/Pt–13% Rh thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2}–10^{-3} mmHg by an Edwards Model ED100 high capactity rotary oil pump, the pressure being measured by a Pirani gauge situated between the trap and the pump. Under these conditions the contact time in the hot zone was estimated to be in the range 1–10 ms.[5] In some cases it was desirable to increase the contact time and this was achieved by packing the furnace tube with 5 cm lengths of silica tubing or a plug of silica wool.

The pyrolysis conditions are quoted as follows: '(weight of material volatilised, furnace temperature, average pressure during the pyrolysis, inlet temperature)'.

Small scale pyrolyses were generally carried out using 25–100 mg of material. After the pyrolysis the system was isolated from the pump and filled with nitrogen gas. The product was then dissolved out of the trap in deuteriochloroform and analysed directly by ^{1}H NMR. By adding the chloroform while the trap was still frozen and keeping the solution cold, volatile or unstable products could be isolated in high yield. Yields were estimated by adding 5–10 mg of a solvent such as cyclohexane or dichloromethane and comparing the NMR integrals. This calibration was estimated to be accurate to ±10%.

In large scale pyrolyses 0.2–1.0 g of material was used and after filling the system with nitrogen the product was dissolved out and purified by the normal methods.

(a) 3,4-*Diphenyl*-2-*oxa*-3-*azabicyclo*[3.2.0]*hept*-3-*ene*-6,7-*dicarboxylic anhydride* **2**. FVP of the title compound (133 mg, 505 °C, $<1 \times 10^{-3}$ mmHg, inlet 127–130 °C) gave no identifiable products; the sample gradually decomposed to form an intractable brown polymeric film within the inlet tube and at the entrance to the furnace. Analysis of the material in the trap (< 10 mg) by IR and TLC showed an absence of any anhydride moiety and benzylideneaniline.

Pyrolysis of the corresponding diacid (101 mg, 600 °C, 1×10^{-3} mmHg, inlet 155 °C) produced similar results with a large amount (66 mg) of charred material remaining in the inlet. Examination of the pyrolysate by NMR spectroscopy showed no identifiable peaks.

(b) 4-*Phenyl*-2-*oxa*-3-*azabicyclo*[3.2.0]*hept*-3-*ene*-6,7-*dicarboxylic anhydride* **3**. FVP of the title compound (8.8 mg, 600 °C, 1×10^{-3} mmHg, inlet 172 °C) over a 30 min period left 0.7 mg residue in the inlet and gave a purple pyrolysate containing 3-phenylisoxazole (71%) and maleic anhydride (49%) by ^{1}H NMR analysis using cyclohexane as internal standard. Preparative TLC on silica gel with dichloromethane–hexane (1:1) as eluent gave 3-phenylisoxazole (29 mg, 56%) whose ^{1}H NMR spectrum; δ_H 6.63 (1 H, d, *J* 2), 7.32–7.48 (3 H, m), 7.73–7.88 (2 H, m) and 8.41 (1 H, d, *J* 2), was identical with a literature spectrum.[31]

(c) 4-(p-*Chlorophenyl*)-2-*oxa*-3-*azabicyclo*[3.2.0]*hept*-3-*ene*-6,7-*dicarboxylic anhydride* **4**. FVP of the diacid of the title compound (89 mg, 600 °C, 1×10^{-3} mmHg, inlet 158 °C) over a period of *ca.* 30–40 min gave a purple pyrolysate containing 3-(*p*-chlorophenyl)isoxazole which was estimated to be formed in 44% yield by analysis of its ^{1}H NMR spectrum: δ_H 6.99 (1 H, d, *J* 2.5), 7.51 (2 H, d, *J* 8.5), 7.92 (2 H, d, *J* 8.5) and 8.82 (1 H, d, *J* 2.5).[32] Preparative TLC on alumina with light petroleum (40–60 °C)–chloroform (10:1) as eluent gave 3-(*p*-chlorophenyl)-isoxazole (21 mg, 39%) as colourless crystals, m.p. 69–71 °C (lit.,[33] 76–78 °C) from light petroleum (60–80 °C).

Pyrolysis of the corresponding dimethyl ester **23** (59 mg, 600 °C, $<1 \times 10^{-3}$ mmHg, inlet 105–110 °C) over a period of *ca.* 1 h gave a purple pyrolysate containing 3-(*p*-chlorophenyl)-isoxazole (52%), dimethyl maleate (36%) and dimethyl fumarate (7%). The yields were determined by GLC analysis (4% APL, 125 °C) and ^{1}H NMR spectroscopy (with added cyclohexane as internal standard).

(d) 4-(p-*Methoxyphenyl*)-2-*oxa*-3-*azabicyclo*[3.2.0]*hept*-3-*ene*-6,7-*dicarboxylic anhydride* **5**. FVP of the dimethyl ester of the title compound (104 mg, 600 °C, 7×10^{-3} mmHg, inlet 90–120 °C) gave a yellow oil whose ^{1}H NMR spectrum showed the presence of an isoxazole ring δ 6.58 (1 H, d, *J* 3) and 8.40 (1 H, d, *J* 3). Preparative TLC on silica gel with diethyl ether–hexane (3:1) as eluent gave 3-(*p*-methoxyphenyl)isoxazole (49 mg, 64%); δ_H 3.82 (3 H, s, OCH_3), 6.58 (1 H, d, *J* 3, 4-H), 6.95 (2 H, d, *J* 9, Ar), 7.77 (2 H, d, *J* 9, Ar) and 8.38 (1 H, d, *J* 3, 5-H) which was identical with the literature spectrum.[34]

(e) 7-*Oxo*-3,4,5,6-*tetraphenyl*-1,2,2a,3,6,6a-*hexahydro*-3,6-*methanobenzocyclobutene*-1,2-*dicarboxylic anhydride* **11**. FVP of the title compound (80 mg, 525 °C, 6×10^{-3} mmHg, inlet 180–195 °C) gave a colourless solid at the liquid nitrogen level of the trap and a yellow liquid at the exit of the furnace. The solid was shown by its ^{1}H NMR spectrum to be maleic anhydride. Preparative TLC of the yellow liquid on silica with diethyl ether–hexane (1:10) as eluent gave 1,2,3,4-tetraphenylbenzene (45 mg, 72%) as a colourless solid, m.p. 189–191.5 °C (lit.,[35] 190–191 °C). Confirmation was given by TLC of the sample on silica with light petroleum (40–60 °C) as eluent against an authentic sample.

FVP at lower temperatures gave the same result but with lower yields: 500 °C (36%); 350 °C (12%); neat thermolysis at 240 °C for 1 h (27%).

(f) 7-*Oxo*-3,6,7-*triphenyl*-1,2,2a,3,6,6a-*hexahydro*-3,6-*methano*-7-*phosphabenzocyclobutene*-1,2-*dicarboxylic anhydride* **12**. Thermolysis of the title compound (600 mg) in a Kügelrohr apparatus at 210 °C under reduced pressure (0.9 mmHg) gave a colourless distillate which gradually solidified. Recrystallisation of the solid from acetone gave *p*-terphenyl (73 mg, 27%), m.p. 209–211 °C (lit.,[36] 210 °C). The remaining undistilled deep orange residue emitted an intense objectionable odour.

FVP of **12** (65.0 mg, 600 °C, $<1 \times 10^{-3}$ mmHg, inlet 177–180 °C) gave *p*-terphenyl in 80% yield by GLC analysis (1% SE 30, 200 °C).

(g) 3,8-*Diphenyl*-3,8-*epoxy*-1,2,2a,3,8,8a-*hexahydrocyclobuta*[b]*naphthalene*-1,2-*dicarboxylic anhydride* **13**. FVP of the title compound (27 mg, 600 °C, 6×1^{-3} mmHg, inlet 200–205 °C) gave a fluorescent yellow solid (19 mg) at the exit of the furnace and a colourless solid (5 mg) at the liquid nitrogen level of the trap. The latter solid was shown by its ^{1}H NMR spectrum to be maleic anhydride. The yellow solid was shown by its ^{1}H NMR spectrum to be 1,3-diphenylisobenzofuran; this was confirmed by comparison with an authentic sample by TLC.

The ^{1}H NMR spectrum also showed that a small amount of 3-oxabicyclo[3.2.0]hept-6-ene-2,4-dione was present in the 1,3-diphenylisobenzofuran component.

(h) 1,2,2a,3,8,8a-*Hexahydro*-3,8-(o-*benzeno*)*cyclobuta*[b]-*naphthalene*-1,2-*dicarboxylic anhydride* **14**. FVP of the title compound (52 mg, 600 °C, 6 × 10^{-3} mmHg, inlet 200 °C) gave a colourless solid (43 mg) at the exit of the furnace. The ^{1}H NMR spectrum of the product showed that a retro-Diels–Alder reaction had taken place to give anthracene and 3-oxabicyclo-[3.2.0]hept-6-ene-2,4-dione. The ^{1}H NMR spectrum showed the yields to be anthracene (65%) and 3-oxabicyclo[3.2.0]hept-6-ene-2,4-dione (35%).

(i) 3,8-*Diphenyl*-1,2,2a,3,8,8a-*hexahydro*-3,8-(o-*benzeno*)*cyclo*-[b]*naphthalene*-1,2-*dicarboxylic anhydride* **15**. Sublimation of the title compound (66 mg, 210–240 °C, 0.1 mmHg) gave a colourless solid (43 mg) which was identical by ^{1}H and ^{13}C NMR spectroscopy with 9,10-diphenylanthracene.

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