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CHEMICAL REPERCUSSIONS OF ORBITAL INTERACTIONS THROUGH BOND AND THROUGH SPACE. EFFECT OF REMOTE SUBSTITUENTS ON THE ADDITION OF NITRENES TO BICYCLIC OLEFINS

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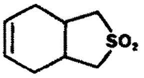
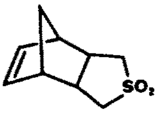
Abstract - The reactivity of a series of bicyclic olefins with nitrenes is profoundly influenced by the nature of remote functional groups. There is a marked lack of reactivity for reactions with carboethoxynitrene as compared to phthalimidonitrene which is distinctly nucleophilic in character. An explanation for the reluctance to form aziridines is offered in terms of orbital interactions between the distant groups and the olefinic bond, making the latter remarkably electron deficient as evidenced by UV-photoelectron spectroscopy. Because of the complexity of the spectra, identification of the Ip associated with the reactive π-centre was made by recourse to *ab initio* configuration interaction calculations for key members of the series.

Although cyclic olefins[1], especially strained systems[2], normally undergo a facile reaction with nitrenes to form aziridines, we have shown[3] recently that the presence of a remote but spatially proximate SO_2 group in a series of unsaturated cyclic sulphones drastically diminishes the susceptibility of the double bond to attack by nitrenes. For example, the bicyclic sulphone (1) showed a remarkable reluctance to react with carboethoxynitrene compared to cyclohexene itself, although the expected aziridine product could be obtained in 40% yield by irradiation of (1) in neat ethyl azidoformate. A marked lack of reactivity was also observed in the expoxidation of these compounds[3].



(1)



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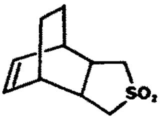
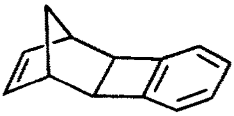


(3)

By recourse to UV- photoelectron spectroscopy (UV-PES), we explained this extraordinary effect in terms of orbital interactions through bonds and/or through space[4] between the sulphone group and the double bond, making the latter remarkably electron deficient. Thus the πIp of the sulphone (1) was found to be 0.57eV higher than that of cyclohexene compared to a difference of 0.62eV between the bridged *endo*-compound (2) and norbornene. A similar but more pronounced effect amounting to 0.75eV was observed for the corresponding ethano-bridged compound (3) with respect to bicyclo [2.2.2] octene. We attributed this enhancement to the sulphone group being forced into closer proximity to the double bond by the bulkier bridge.

Chemical repercussions arising from proximity affects of this type are sparse[5], despite numerous studies by theoretical[6] and spectroscopic[4,7] investigators. Most examples are of a negative nature resulting in decreased reactivity, but in some cases enhanced rates of reaction are observed. Perhaps the most dramatic of these is the Birch reduction of norbornadiene and related compounds, *e.g.* (4)[8] and (5),[9] which occur much faster than norbornene. Orbital interactions are also thought to be responsible for the eightfold increase of reactivity of (6; X=0) towards oxymercuration as compared to (6; X=CH_2).[10]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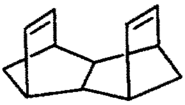
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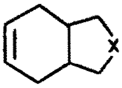


(6)

In the present study we extend our investigation into the influence of remote SO_2 groups on the reactivity of isolated double bonds to show that the same dampening effect towards nitrene attack is also manifested by other heteroatomic functionalities in the series of bicyclic olefins (8) -(21). As previously we have sought quantitative information on the extent of orbital interactions (through bond and through space) in this series of compounds by using UV-PES. Because of the complexity of the spectra, identification of the ionisation potential (Ip) relevant to the olefinic double bond was made by recourse to *ab initio* configuration interaction (CI) calculations, at least for key members of the series.

METHODS AND RESULTS

(i) UV-photoelectron spectroscopy. Photoelectron spectra of compounds (9)-(20) were determined on a Perkin-Elmer PS16 spectrometer as previously described[3] and are shown in Figure 1. The corresponding Ip values and assignments are recorded in Table 1. From concurrent investigations

Table 1 Vertical Ionisation potentials (eV) and assignments for compounds (9)-(20)

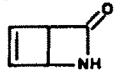
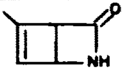
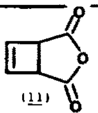
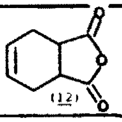
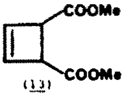
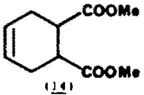
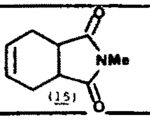
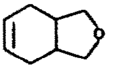
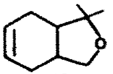
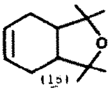
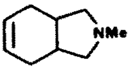
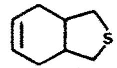
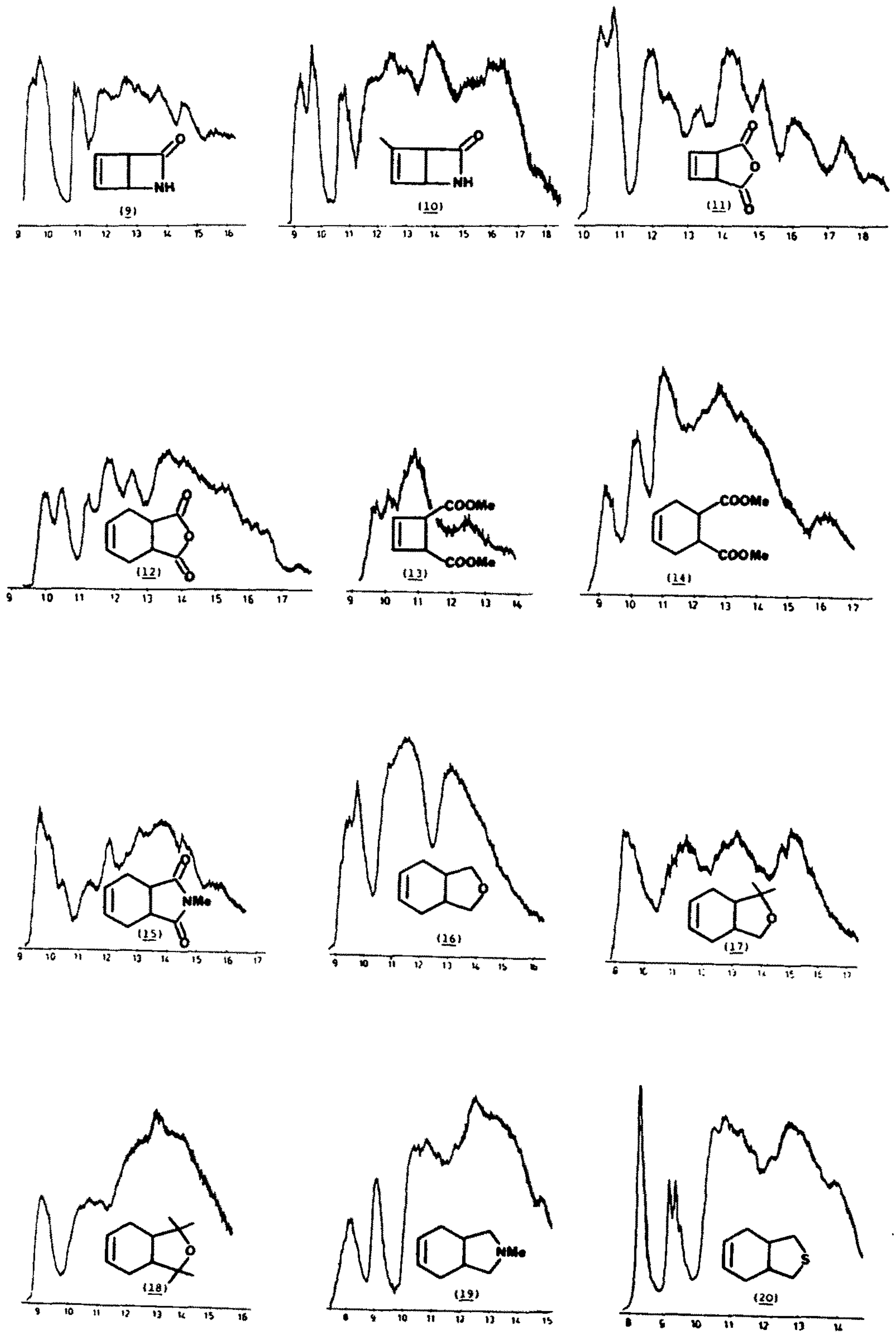
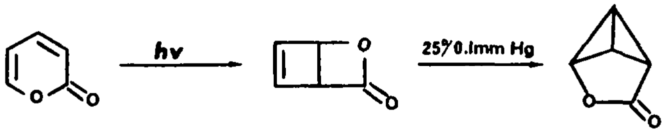
 (9)	 (10)	 (11)	 (12)	 (13)	 (14)
9.39 LP_O	9.22 LP_O	10.49 π	10.00 π	9.76 π	9.25 π
9.9 LP_{NCO}	9.7 LP_{NCO}	10.95 LP_O^-	10.6 LP_O^-	10.00 LP_O	10.1 LP_O
11.0 π_{CC}	10.8 π_{CC}	11.8 LP_O^+	11.3 LP_O^+	10.58 σ	11.06 σ
 (15)	 (16)	 (17)	 (18)	 (19)	 (20)
9.62 π	9.5 π	9.29 π	9.03 π	8.20 LP_N	8.22 LP_S
10.00 LP_N	9.95 LP_O	9.59 LP_O	9.25 LP_O	9.1 π	9.2 π
10.5 LP_O	10.99 σ	10.7 σ	10.25 σ	10.53 σ	10.67 σ

Fig. 1 HeI photoelectron spectra of compounds (9)-(20) in counts/s. *vs* IP (eV)



into the flash-vacuum pyrolysis of many compounds of this type we were aware of the dangers of thermal decomposition; thus all compounds were studied at the lowest temperature practicable for a high counting rate without any noticeable decomposition.

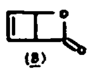
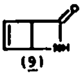
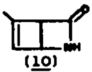
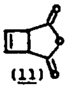
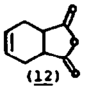
In the case of 5-oxabicyclo[2.2.0]hex-2-en-6-one (8), the major product from the photolysis of α-pyrone (7), a photoelectron spectrum has been reported[11] previously, although the lactone (8) is notoriously unstable, yielding tricyclo [$2^{3,6}$.1.1.0]pyran-2-one (22) even in a molecular still at 25°/0.1mm Hg[12]. Because the possibility of this rearrangement was overlooked at the time[11] we have studied the theoretical spectra of both (8) and its thermal isomer (22).



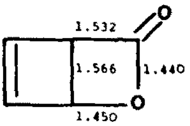
(7) (8) (22)

(ii) *Ab initio* molecular orbital calculations. Two Gaussian atomic orbital basis sets were used (a) a scaled best atom (7s3p/3s) contracted to [2s1p/1s] for (C,N,O/H) respectively, as used in our previous work[3], and (b) the Dunning double-zeta (9s5p/4s) contracted to [4s2p/2s][13]. In the first instance the SCF calculations using basis (a) were carried to the SCF level for molecules (8) - (12), and some open shell calculations of lowest cationic states of each symmetry were obtained for molecules (8), (9) and (10). In the next phase, the molecules (8)-(11) and (22) were studied at the basis (b) level, and the calculations were taken directly from the SCF to CI level. The latter used the ATMOL-3/MRDCI[14] system of programs mounted on the CRAY-1S computer (ULCC), and used a multi-reference basis as follows:- the core and inner valence shell electrons were frozen, and the configurations generated from the 10 highest occupied valence shell orbitals into the lowest 22 virtual orbitals were obtained. The reference set consisted of up to 8 reference configurations (Table 2), and the first group of 3-6 roots of the CI process were obtained. This was sufficient to be correlated with the low Ip (8-13 eV) region of the photoelectron spectrum, and thus *inter alia* assigns the Ip attributable to ionisation from the classical $\pi_{C=C}$ orbitals of (8) - (11).

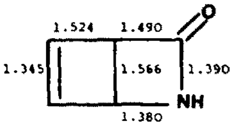
Table 2 SCF orbital energies for the active CI set

 (8)	Minimal Basis, 11.18, 12.69, 12.96, 13.18, 15.18, 15.80, 16.26, 17.81, 18.54, 19.16, 19.87. Double Zeta, 10.76, 12.44, 12.73, 12.91, 14.90, 15.50, 16.03, 17.60, 18.69, 19.20, 19.63.
 (9)	Minimal Basis, 10.39, 10.56, 12.06, 12.71, 14.24, 14.48, 15.21, 16.91, 17.44, 19.02, 19.59.
 (10)	Minimal Basis, 10.21, 10.38, 11.73, 12.56, 13.95, 14.04, 15.09, 15.66, 16.17, 16.93, 17.28, 18.73. Double Zeta, 10.04, 10.63, 11.78, 12.28, 13.77, 13.88, 15.29, 15.41, 15.98, 16.85, 17.45, 18.55, 18.82.
 (11)	Minimal Basis, a', 11.68, 13.57, 13.74, 15.55, 16.86, 17.45, 18.92; a'', 13.05, 14.41, 16.64, 17.56, 18.57. Double Zeta, a', 11.24, 13.21, 13.39, 15.24, 16.63, 17.19, 18.89; a'', 12.88, 13.88, 16.17, 17.35, 18.57.
 (12)	Minimal Basis, a', 10.83, 13.26, 13.56, 14.49, 16.02, 16.55, 17.41, 17.95; a'', 12.81, 13.33, 15.36, 16.14, 16.81, 17.85.
 (22)	Double Zeta, a', 10.49, 12.75, 15.27, 16.68, 17.56, 18.53; a'', 11.75, 13.37, 14.87, 18.30.
	Double Zeta, a_1, 9.60, 15.89, 19.04, 21.43, 33.77; b_1, 12.75, 21.43; b_2, 14.17, 16.04, 25.47; a_2, 12.04.

(iii) Molecular structures In the absence of experimental structures for the compounds in question, it was necessary to construct geometries from appropriate molecular fragments. Thus for (8) - (11), cyclobutene[15] was fused, at the interplanar angle of Dewar benzene[16] to propiolactone[17], azetidinone[18] and succinic anhydride,[19] respectively. In all cases the "fused" bonds were taken as averages of the pair of monocyclic systems. Typical structures are (8a) and (9a).



(8a)



(9a)

In a similar way, fusion of cyclohexene with succinic anhydride gave the bicyclic anhydride (12). From electron diffraction studies, cyclohexene adopts a half-chair conformation[20] but inspection of Dreiding models shows that fusion of this conformation with the anhydride leads to marked steric hindrance which is relieved in a boat conformation with a co-planar arrangement of C_3-C_6.

The structure of the tricyclic lactone (22) was obtained by condensation of the bicyclobutane structure[21] with that of methyl formate[22]. Curiously this was accomplished with less angle distortion than the corresponding modification of the benzvalene structure[23]; the two interplanar angles differ by 16°.

(iv) Assignment of photoelectron spectra

(a) Bicyclo[1.1.0]butane. Both He(I) & He(II) spectra have been reported[24,25] for bicyclo[1.1.0]butane with the former showing broad bands at 9.25, 11.5, 13.0, 14.5, 16.9 & 17.05 eV. The relatively small size of this molecule made it practicable to carry out a larger CI study than was required for the present work, leading to the results in Table 3. In general the agreement between

Table 3 SCF and CI results for ground and ionised states of bicyclo[1.1.0]butane

State	Configns.	Ref Configns	Energy		Principal Configurations	
			Total (-E) (a.u.)	Ionisation (eV)	Coefficient	Occupancy (Differences)
X^1A_1	1 (SCF-DZ)	-	154.7862	-		$1\text{-}7a_1^2$, $1\text{-}3b_1^2$, $1\text{-}4b_2^2$, $1a_2^2$
X^1A_1	5725	1	155.0388	-	0.912	SCF
					+0.003	$-7a_1^2$, $+5b_1^2$
1^2A_1	14272	3	154.7119	8.90	0.898	$-7a_1$
2^2A_1	14272	3	154.5057	15.51	0.883	$-6a_1$
3^2A_1	14272	3	154.4044	17.26	0.870	$-5a_1$
1^2B_1	16113	3	154.6133	11.58	0.881	$-3b_1$
2^2B_1	16113	3	154.3973	17.46	0.623	$-3b_1$, $+5b_1^2$, $-7a_1^2$
					+0.198	$-2b_1$
3^2B_1	16113	3	154.3383	19.06	0.637	$-2b_1$
					+0.177	$-3b_1$, $+5b_1^2$, $-7a_1^2$
1^2A_2	5904	1	154.6236	11.30	0.897	$-1a_2$
1^2B_2	26149	5	154.5635	12.93	0.887	$-4b_2$
2^2B_2	26149	5	154.4997	14.67	0.878	$-3b_2$
3^2B_2	26149	5	154.3392	19.04	0.799	$-7a_1$, $-1a_2$, $+5b_1$
4^2B_2	26149	5	154.2895	20.39	0.725	$-7a_1$, $-1a_2$, $+5b_1$
					+0.064	$-2b_2$

the observed and calculated Ip values is good throughout the above range (± 0.2 eV generally); the work confirms the HOMO as $7a_1$, a pseudo π-level, in agreement with earlier semi-empirical work[26]; several changes of order and groupings occur (Table 4) relative to this earlier study, which was relatively non-rigorous. A shake-up peak, not yet observed, was computed at 17.5 eV corresponding to the process $7a_1{}^2 3b_1{}^2 \rightarrow 3b_1{}^1\ 5b_1{}^2$; this is a "π-π*" type process. Unusually, in the light of its high energy, the 3^2B_1 state even at 19 eV is still recognisably a 1-electron (Koopmans') process.

Table 4 Assignment of the UV-PES for bicyclo[1.1.0]butane

State	Ionisation Potential (eV)		Previous Assignment (Koopmans' Theorem)
	Calc. by CI	UV-PES	
1^2A_1	8.90	9.25	1^2A_1
1^2A_2	11.30	11.5	$1^2A_2 + 1^2B_2$
1^2B_1	11.58		
1^2B_2	12.93	13.0	1^2B_1
2^2B_2	14.67	14.5	2^2A_1
2^2A_1	15.50		2^2B_2
3^2A_1	17.26	17.05	3^2A_1
2^2B_1 (shake-up)	17.46		
3^2B_1	19.04		
3^2B_2	19.06	19.1	2^2B_1
4^2B_2	20.39		

(b) 5-Oxabicyclo[2.2.0]hex-2-en-6-one(8) and tricyclo [$2^{3,6}$.1.10] pyran-2-one(22). Comparison of the Ip values of methyl acetate (10.48, 11.16 eV)[27] and β-priopiolactone (10.78, 11.30 eV)[31] shows that the two lowest Ip's are stabilised by about 0.2 eV in the cyclic compound; in the limiting situation of no interaction between the two rings, compound (8) would then have Ip values near 9.4 ($\pi_{C=C}$), 10.78(LP_O) and 11.3 eV (π_{NOO}). The spectrum reported by Schweig *et al*[11] for (8) has values at 10.06, 11.02 and 11.48 eV. Whilst the last two are compatible, the large effect upon $\pi_{C=C}$ is surprising, especially since in the corresponding amide (*vide infra*) the effect was about 0.2 eV or less. The question of whether the reported spectrum [11] related to the tricyclic lactone (22) rather than (8) seemed open. The CI-computed Ip values (Tables 5 & 6) do not entirely resolve the issue as shown below, presumably because one or both of the compounds (8) and (22) differ significantly from their assigned geometric structure although the agreement with experiment is excellent for the amides (9) and (10).

The doublet states for the bicyclic lactone (8) showed errors in the first three Ip values of about +0.5 eV, *i.e.*, too high; however, a gap between Ip_4 and Ip_5 of about 1.8 eV was predicted, and this corresponds to high counting rates between 12 & 14 eV in the observed spectrum. On the other hand, the computed spectrum for the isomeric tricycle showed two Ip values near 13.5 eV, both of which are about 0.5 eV too low for Ip_1 to Ip_3 when compared with the reported spectrum. Given the statement[11] that "the thermal behaviour of these compounds...[5-oxa-bicyclo[2,2,0] hex-2-en-6-one (8) and its progenitor 2H-pyran-2-one (7)]..up to 800°C under the conditions of variable temperature photoelectron spectroscopy (VTPES)", we have to conclude that (8) would certainly not be present over most of the temperature range; this, together with the present results, strongly indicates that the lower temperature spectrum of reference[11] is actually that of compound (22).

Table 5 SCF and CI results for ground and ionised states of 5-oxabicyclo[2.2.0]hex-2-en-6-one (8)

State	Configns	Ref Confign	Energy		Principal Configurations	
			Total(-E) (a.u.)	Ionisation (eV)	Coefficient	Occupancy (Differences)
X^1A'	1(SCF-MB)	-	340.2759	-	1	1-25a'
	1(SCF-DZ)	-	341.1335	-	1	1-25a'
$1^2A'$	1(SCF-MB)	-	339.8966	10.32	-	$-\sigma$-LP(O)
$2^2A'$	1(SCF-MB)	-	339.8922	10.44	-	$-\pi$(cc)
$3^2A'$	1(SCF-MB)	-	339.8680	11.10	-	$-\pi$-LP'(OCO)
X^1A'	16984	3	341.2194	-	0.946	SCF
$1^2A'$	16317	5	340.8329	10.518	0.904	-25a'
$2^2A'$	16317	5	340.7928	11.609	0.748	-24a'
$3^2A'$	16317	5	340.7786	11.995	0.607	-23a'
$4^2A'$	16317	5	340.7731	12.146	0.481	-22a'
$5^2A'$	16317	5	340.7062	13.964	0.887	-21a'

Table 6 SCF and CI results for ground and ionised states of tricyclo[2^{3,6}.1.1.0]pyran-2-one (22)

State	Configns.	Ref Confign.	Energy		Principal Configurations	
			Total(-E) (a.u.)	Ionisation (eV)	Coefficient	Occupancy (Differences)
X^1A'	1(SCF-DZ)	1	341.1032	-	1	1-19a', 1-6a''
X^1A'		1	341.2102	-	0.949	SCF
$1^2A'$		8	340.8573	9.60	0.881	-19a'
$2^2A'$		8	340.8024	11.10	0.843	-18a'
					+0.027	-18a', -5a'', +7a''
$3^2A'$		8	340.7186	13.38	0.832	-17a'
$4^2A'$		8	340.6527	15.17	0.870	-16a'
$5^2A'$		8	340.6394	15.53	0.820	-15a'
					+0.028	-15a', -6a'', +7a''
$1^2A''$		7	340.8294	10.36	0.877	-6a''
$2^2A''$		7	340.7699	11.98	0.861	-5a''
$3^2A''$		7	340.7077	13.67	0.862	-4a''
$4^2A''$		7	340.6283	15.84	0.725	-3a''
					+0.081	8a'' -(7a'')^2
					+0.020	-5a'', -6a'', +7a''

(c) 5-Azabicyclo[2.2.0]hex-2-en-6-one(9)and its 2-methyl analogue (10). In contrast to the lactone (8), both these compounds are thermally stable and show two well-defined bands between 9 and 10 eV, another one near 11 eV and a relatively similar envelope up to 15 eV. A band close to 16 eV is also evident in the spectrum of (10) for the Me group Ip's arising from mixing of the E pair of levels in C_{3v} with the ring. Because the photoelectron spectrum of azetidinone is not known, the effect of fusion with cyclobutene cannot be determined from the Ip values. If an analogy between cyclic and acyclic systems can be made, then the amide (9) and lactone (8) can perhaps be compared with *N*-methyl acetamide and methyl acetate^{27}, respectively. An estimate of the Ip values of azetidinone (9.8 & 10.2 eV) can be obtained by incorporation of the difference between *N*-methyl acetamide (9.68 π_2, 9.85 n_O) and methyl acetate^{27} into propiolactone; the values are sufficiently close to cyclobutene (9.43 eV^{28}) for the assignment of the spectra of the amides (9) & (10) to be non-trivial. Open shell SCF-MB calculations on the unsubstituted amide (9) suggested that the $\pi_{C=C}$ level was the most heavily bound of the first 3 orbitals with two, nearly equally spaced, amide orbitals being ionised more easily (ø-LP$_O$ being the HOMO, and followed by π_{NCO}). The double-zeta (DZ) calculations (Table 7) reversed this order of binding energy to $\pi_{C=C} < \pi_{NCO} < \pi LP_O$, and this was confirmed by the DZ-CI. In fact the numerical agreement with the photoelectron spectra between the first few doublet states down to about 13 eV was excellent for both (9) and (10); all were clearly identified as Koopmans' type states, *i.e.* ionisation from a single SCF orbital is the dominant term. Thus the comparison with *N*-methyl acetamide $\pi_2 < LP_O$ is seen to hold in the present compounds. The other amide O-C-N π-bonding orbital (π_1 in the usual terminology) is computed as Ip$_6$ at 13.0 eV. Brundle *etal*[29] have assigned this state to Ip$_4$ at 14.75 eV in formamide (Koopmans' theorem calculations), but the more recent Greens' Function calculations[30] suggest 14.36 eV (Ip$_3$); the latter is more compatible with electron release by the bridging groups in the present compounds (9) and (10).

Table 7 SCF and CI results for the ground and ionised states of 5-azabicyclo[2.2.0]hex-2-en-6-one (9) and its 2-methyl analogue (10)

State	Configns.	Ref Confign.	Energy (-E)		Principal Configurations	
			Total (a.u.)	Ionisation (eV)	Coefficient	Occupancy (Differences)
Molecule (9)						
X^1A'	SCF-MB	1	320.5162	-	1	1-25a'
$1^2A'$	SCF-MB	1	320.2189	8.09		-LP(O)
$2^2A'$	SCF-MB	1	320.1875	8.94		-LP(NCO)
$3^2A'$	SCF-MB	1	320.1514	9.93		- (CC)
Molecule (10)						
X^1A'	SCF-MB	1	359.4692	-	1	1-29a'
X^1A'	SCF-DZ	1	360.3452	-	1	1-29a'
X^1A'	30827	3	360.4142	-	0.958	SCF
	30827				+0.008	-29a' + 30a'
$1^2A'$	32199	6	360.0677	9.43	0.797 +0.111	-29a' -27a'
$2^2A'$	32199	6	360.0588	9.67	0.882	-28a'
$3^2A'$	32199	6	360.0238	10.62	0.728 +0.136	-27a' -29a'
$4^2A'$	32199	6	359.9891	11.57	0.888	-26a'
$5^2A'$	32199	6	359.9576	12.42	0.764 +0.049 +0.022	-24a' -25a' -26a'
$6^2A'$	32199	6	359.9350	13.04	0.859	-25a'

(d) Cyclobutene-3,4-dicarboxylic acid anhydride (11) and *cis*-1,2,3,6-tetrahydrophthalic anhydride (12) The first Ip of the 4-membered ring anhydride (11) occurs at 10.49 eV, substantially higher than that of cyclobutene (9.43 eV[28]) but lower than the lone pair levels of succinic anhydride (10.8 and 11.6 eV[32]). From Table 8 the *ab initio* calculations at both SCF radical cation and DZ-CI level show that the first Ip is largely from the local $\pi_{C=C}$ bond. The Ip values in the 11-12.5 eV region are all dominated by the anhydride moiety whilst those from 10-14 eV follow the DZ-SCF orbital ordering, being Koopmans' type states. As in the lactones (8) and (22), the calculated Ip values are not in such good agreement as for the amides (9) and (10); again this suggests that the strong interaction between the two rings has had a more marked effect upon the geometry.

Table 8 SCF and CI results for ground and ionised states of cyclobutene-3,4-dicarboxylic acid anhydride (11)

State	Configns	Ref Confign	Energy		Principal Configurations	
			Total(-E) (a.u.)	Ionisation (eV)	Coefficient	Occupancy (Differences)
$X^{1}A'$	1(SCF-MB)	-	452.7118	-	1	1-19a', 1-13a''
	1(SCF-DZ)	-	453.8996	-	1	1-19a', 1-13a''
$1^{2}A'$	1(SCF-MB)	-	452.3177	10.72	-	-π(cc)
$1^{2}A''$	1(SCF-MB)	-	452.2612	12.26	-	-σ-LP(CO)
$X^{1}A'$	11116	3	453.9847	-	0.937	SCF
$1^{2}A'$	15177	5	453.5900	10.74	0.902	-19a'
$2^{2}A'$	15177	5	453.5332	12.29	0.851	-18a'
$3^{2}A'$	15177	5	453.5214	12.61	0.885	-17a'
$4^{2}A'$	15177	5	453.4679	14.06	0.865	-16a'
$1^{2}A''$	20287	6	453.5598	11.56	0.886	-13a''
$2^{2}A''$	20287	6	453.5055	13.04	0.895	-12a''
$3^{2}A''$	20287	6	453.4176	15.43	0.868	-11a''

For the 6-membered ring anhydride (12), the MB-SCF calculations showed that the preferred conformation of the cyclohexene portion was a boat rather than a half-chair or planar structure. As a result, the proximity of the two groupings is increased in the preferred conformation. The HOMO, 23a', is heavily localised in the hexene moity as expected (*cf.* π Ip = 9.12 eV for cyclohexene[28]); this is followed by π_{OCOCO} and LP_{CO}, a similar order to that observed in the 4-membered compound (11). Comparison of the two sets of calculations suggests the following assignments: (i) $\pi_{C=C}$; 10.49 (11), 10.00 (12); (ii) π_{OCOCO}, 10.95 (11), 10.6 (12); LP_{CO}, 11.8 (11), 11.3 (12). This overall raising of Ip values for (11) with respect to (12) presumably reflects the net increase in strain in the former molecule.

(e) *cis*-Dimethyl cyclobutene-3,4-dicarboxylate(13) and *cis*-dimethyl 1,2,3,6-tetrahydro-phthalate (14). Steric constraints dictate that the bulky *cis*-ester groupings cannot lie co-planar, making a flexible system with interplanar angles nearly perpendicular to the local portion of the cycloalkene most likely. In both cases, the first Ip values fall between those for the corresponding hydrocarbons and their bicyclic anhydrides. Clearly, a co-planar arrangement of the ester groupings is unnecessary to cause a through-bond (inductive) effect upon the πIp, which must be assigned to IP_1 for both (13) and (14).

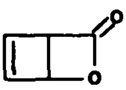
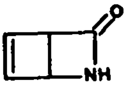
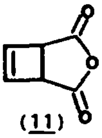
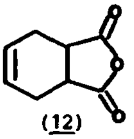
(f) 8-Oxabicyclo[4.3.0]non-3-ene (16) and related compounds (17) - (20). Direct comparison of recorded first Ip values for each of these molecules with those of cyclohexene (9.12 eV)[28] and the corresponding mono-cyclic compounds, *i.e.*, tetrahydrofuran (9.65 eV)[33], *N*-methylpyrrolidine (8.41 eV)[34] and tetrahydrothiophen (8.40 eV)[35] shows that cross-ring interactions are significant. In the case of the *N*-methyl compound (19) and its thia-analogue (20) the π-LP levels of the monocyclic species are the same (8.4 eV), and both are shifted to 8.2 eV by fusion to cyclohexene. When the second Ip of both compounds are compared with cyclohexene itself, a much smaller shift to higher binding energy is observed, *e.g.* 9.12 to 9.2 eV for (20). Because the sharper LP levels make small shifts more accurately determined, we consider the aforementioned difference of 0.2 eV to be evidence of through-space interactions in both cases. However, the present results for oxa-analogue (16) show that two mechanisms occur; although a lowering of $\pi_{C=C}$ might have been expected from interaction with the more tightly bound LP_O of tetrahydrofuran,[33] the contribution of the O_{2p} density to the $\pi_{C=C}$ MO leads to a binding energy increase, owing to the higher binding energy of O_{2p} relative to C_{2p}. In principle, we expect to see the reverse effect on LP_O of the bicyclic ether (16), relative to LP_O of tetrahydrofuran, namely a shift of LP_O to lower binding energy as a result of the $2p_C$ contribution. However, the position is more complex, since the actual LP_O level of tetrahydrofuran arises from interactions with two pairs (α and β) of CH_2 group orbitals. The β-pair do not exist in (16) and there is some difficulty in estimating the effective baseline for the LP_O, arising solely from interaction with the α-set. The values for dimethyl ether (10.04 eV) and water (12.61 eV) give limiting values of one and no CH_2 interactions. The value observed in (16) is lower than either pair. Thus instead of the normal effect of orbital interactions in hydrocarbons (symmetric combination stabilised; anti-symmetric combination de-stabilised), we find that the two levels are closer. Long-range oxygen participation has previously been proposed for (16) as an explanation for its enhanced electrophilic addition reactions relative to the corresponding carbon compound.[10]

The position is similar for the bicyclic imide (15) in relation to *N* -methyl succinimide and cyclohexene. The photoelectron spectrum of *N*-methyl succinimide has been assigned as 10.0 (LP_O^-) and 10.7 eV (LP_O^+)[36]; only the symmetric combination LP_O^+ is able to combine with $\pi_{C=C}$; *i.e.* this is an interaction of local $\pi_{C=C}$ with the sigma lone pair combination. Thus we expect LP_O^- to be relatively unchanged in the bicyclic compound (15) and this is found to be the case (10.0 eV). Mixing of the $LP_O^+/\pi_{C=C}$ levels then perturbs each, but the heavy $2p_O$ contribution of the former is diluted by $2p_C$ leading to a shift to lower binding energy of LP_O^+, and to higher binding energy for $\pi_{C=C}$, as observed.

(v) Mulliken analyses As seen from Table 9 the $\pi_{C=C}$ orbital ($2b_1$) of cyclobutene is about 87% localised in the double bond, the remainder being attributable to the CH_2 groups. In contrast, the bicyclic lactone (8) has the $\pi_{C=C}$ density spread through several orbitals, but largely in 25a' and 24a'; it is clear that each of these are linear combinations of $\pi_{C=C}$ and lactone orbitals, and the highest density of $\pi_{C=C}$ is 60% in 25a'.

A similar phenomenon occurs with the corresponding amide (9) and the bicyclic anhydrides (11) and (12). Overall heteroatom groupings are net acceptors of about 0.2 to 0.35 e, but this masks the more dramatic effect on the $\pi_{C=C}$ orbitals. In view of the O/N atom density in the orbitals of largely $\pi_{C=C}$ character, the Ip of the latter will be shifted to higher binding energy. This position is reminiscent of the bicyclic sulphones of our previous paper.[3]

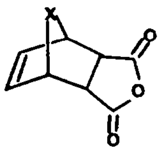
Table 9 Mulliken analysis of some molecular fragments

	Fragment	$2(CH_2)$	CH=CH		
	Population Total	15.9718	14.0282		
	$2b_1$ (π-C=C)	0.1285	0.8715		
 (8)	Fragment	CH-CH	CH=CH	OCO	
	Population (Total)	13.7380	13.9176	22.3445	
	π-Orbitals, 25a'	0.1152	0.5997	0.2849	
	π-Orbitals, 24a'	0.2074	0.2561	0.5360	
 (9)	Fragment	CH-CH	CH=CH	OCNH	
	Population (Total)	13.8534	13.9435	22.2030	
	π-Orbitals, 23a'	0.0584	0.4835	0.4581	
	π-Orbitals, 24a'	0.1102	0.3832	0.5064	
 (11)	Fragment	CH-CH	CH=CH	OCOCO	
	Population (Total)	13.9406	13.8818	26.1776	
	π-Orbital, 19a'	0.0842	0.7274	0.1883	
 (12)	Fragment	$2(CH_2)$	CH-CH	CH=CH	OCOCO
	Population (Total)	15.8798	13.9482	13.9910	36.1797
	π-Orbital	0.1328	0.0216	0.8336	0.0118

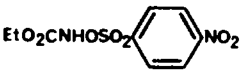
REACTIVITY STUDIES

In the previous paper,[3] we reported that the ease with which nitrenes form aziridines from a series of bicyclic olefins, where distant sulphonyl groups are present, was markedly variable . A reasonable correlation was found to exist between the reactivity of the olefinic groups and their π-ionisation potentials which were all very high with respect to comparison olefins. In the present paper the main objective was to determine whether the presence of orbital interactions in the present molecules, as evidenced by UV-PES, are sufficiently strong to cause a similar lack of reactivity towards both carboethoxynitrene and phthalimidonitrene. The latter nitrene is postulated[37] to be nucleophilic, an hypothesis that is supported by the much higher yield of aziridine obtained from dimethyl cyclobutene-1,2-dicarboxylate (35%)[38] than from 3,4-dichlorocyclobutene (6%).[39] However, both nitrenes form aziridines with cyclobutene[39] (π Ip = 9.43 eV), but in markedly different yields, *i.e.* 2% and 20%, respectively. Much better yields are obtained from the addition to the less strained double bond of cyclohexene (πIp = 9.12 eV[28]) which reacts to the extent of 57% with carboethoxynitrene[40] and 40% with phthalimidonitrene[37]. In the case of cyclopentene (πIp = 9.18 eV[28]), the corresponding reaction with phthalimidonitrene occurred in 49% yield compared to 27% and 24% with cycloheptene (πIp = 9.04 eV[28]) and cyclo-octene (πIp = 8.98 eV[28]), respectively.

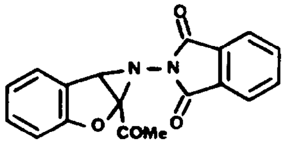
Nitrenes. Carboethoxynitrene was produced by base-induced α-elimination of ethyl *p*-nitrophenylsulphonyloxycarbamate (Lwowski's reagent) (23) under homogeneous conditions[40]. Phthalimidonitrene was in most cases generated by oxidation of *N*-aminophthalimide with lead tetra-acetate (LTA)[37]. Where the use of LTA was considered undesirable because of concomittant formation of acetic acid, the nitrene was produced by thermolysis of Jones' *N*-phthalimidoaziridine (24) which is itself prepared by LTA oxidation of *N*-aminophthalimide in the presence of 2-acetylbenzofuran.[41]



(21)



(23)



(24)

DISCUSSION

As is evident from Table 10, significant differences are observed in the reactivity of the nitrenes towards the present bicyclic olefins*. In marked contrast to the reactions with phthalimidonitrene, those involving carboethoxynitrene gave no detectable aziridine product with compounds of relatively high π-ionisation potential. This sharp difference in reactivity presumably reflects the electronic factors inherent in the two nitrenes. Whereas phthalimidonitrene is distinctly nucleophilic in character, powerfully electron-withdrawing groups render carboethoxynitrene an electrophilic species whose reactivity is diminished to the point where it will only add to electron-rich double bonds. For example, cyclohexene with its much lower πIp of 9.12 eV gives a good yield of aziridine with carboethoxynitrene,[40] whereas no reaction occurred with the bicyclic anhydride (12) which is substantially more electron deficient as evidenced by its πIp of 10.00 eV. A similar lack of reactivity towards carboethoxynitrene is observed with *endo*-norbornylene-5,6-dicarboxylic anhydride (21; X=CH_2) for which orbital interactions are invoked[42] to account for its high πIp of 9.85 eV. By comparison, the corresponding reaction with norbornene (πIp = 8.97 eV[43]) itself leads to aziridine formation in 20% yield. As in the case of the unsaturated bicyclic sulphones (1)-(3) which are also inert towards carboethoxynitrene[3], aziridines could be obtained from both of the anhydrides (12) and (21; X=CH_2) in moderate-to-good yields by reaction with ethyl azidoformate either thermally or photochemically

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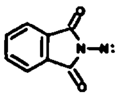
* We recognise that the yield from these reactions cannot be taken as a true measure of their rate, but it does provide a rough indication and in particular a very low or zero yield in any reaction indicates a very slow rate.

Table 10 Formation of aziridines from the bicyclic olefins (8)-(21) and some comparison olefins (% yields)

		Reaction conditions		
Compound	πIp eV		EtO_2CN:	EtO_2CN_3 hν
(8)	10.06	10	NR[a]	NR
(9)	9.39	-	-	-
(11)	10.49	NR	NR	NR
(12)	10.00	13	NR	32[d]
(13)	9.76	35[38]	NR	-
(14)	9.25	17	28	-
(15)	9.62	28	-	-
(16)	9.50	24	-	-
(17)	9.29	18	-	-
(18)	9.03	15	-	-
(19)	9.1	NR	-	-
(20)	9.2	NR	-	-
(21) $X=CH_2$[b]	9.85	NR	NR	64 (43[e])
(21) $X=CH_2CH_2$[b]	-	-	NR	23
(21) X=O[c]	-	NR	NR	26
Norbornene	8.97	25	20	89
Cyclobutene	9.43	20	2	-
Cyclohexene	9.12	40	57[40]	62

[a] NR = no aziridine formed; only nitrene by-products were isolated. [b] endo-Configuration. [c] exo-Configuration. [d] Isolated as diester. [e] Boiling under reflux in dry CCl_4.

These reactions probably proceed by cycloaddition of the azide[1,44] followed by loss of nitrogen from the resulting triazoline. Their success in producing an aziridine, in contrast to the failure of nitrene addition, accords with the assumption that a cycloaddition process is less dependent upon electrophilicity in the attacking reagent. Nonetheless we should emphasise that the sensitivity of the anhydride function to hydrolysis* restricts the applicability of the azide method as a preparative route to aziridines. For example, irradiation of the anhydrides (11) and (12) with ethyl azidoformate probably did result in aziridine formation, but attempts to purify the products by flash chromatography or by sublimation led to hydrolysis and decomposition, respectively. This contrasts with the bridged anhydrides (21) whereupon, the addition of ether to the photolysis mixture led to crystallisation of the desired aziridines. A good yield of aziridine could also be obtained in the case of (21; $X=CH_2$) by heating the compound with ethyl azidoformate in boiling carbon tetrachloride, but (11), (12) and (21; X = O) proved to be inert to these reactions conditions, whilst (21; $X = CH_2CH_2$) afforded only small amounts of the expected product.

Despite a greater propensity to react with electron-deficient olefins, phthalimidonitrene failed to add to the double bond of the bicyclic anhydride (11) with its exceptionally high πIp value of 10.49 eV, nor would it react with the anhydrides (21) ($X=CH_2$; πIp = 9.58 eV[42]) and(21; X=O). The possibility that these failures resulted from a weak but diverting interaction between the nitrene and the anhydride function itself was discounted by the isolation of aziridines from the reaction with the anhydride (12) (πIp = 10.00 eV) and the lactone (8) (πIp = 10.06 eV), albeit in 13 and 10% yield, respectively. Additionally, we found that aziridine formation with the more reactive bicyclic ether (16) (πIp = 9.50 eV), which occurred to the extent of 24%, proceeded

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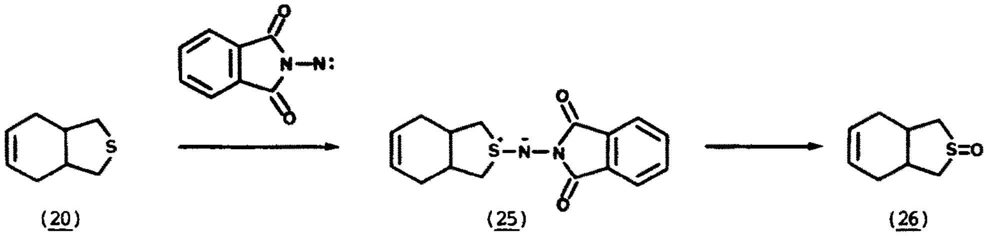
* Hydrolysis also prevented reactions with carboethoxynitrene under phase-transfer conditions[45], a method that we found to be extraordinarily efficient for unsaturated cyclic sulphones[3].

normally in the presence of an equimolar amount of succinic anhydride. The same reaction with the thia-analogue (20), gave after chromatography on alumina, the corresponding sulphoxide (26) as the only isolable product in 28% yield. Since it is known[46] that sulphides are efficient nitrene traps, it is likely that in this case, the reactive site is the sulphur rather than the olefinic bond. Subsequent hydrolysis of the resulting sulphilimine (25) then leads to the observed product. We were also unable to obtain an aziridine from the related reaction of the *N*-methyl



(20) (25) (26)

amino compound (19) with phthalimidonitrene, irrespective of whether the latter was generated by LTA oxidation of *N*-aminophthalimide or from the thermolysis of the *N*-phthalimidoaziridine (24). Both reactions gave unidentifiable products, intimating that reaction had occurred preferentially once again at the more electron-rich amine function.

For those bicyclic olefins that did react with phthalimidonitrene, competition experiments showed a decrease in reactivity as compared to cyclohexene. It is interesting to note that the bicyclic ether (16) (k_{rel} = 0.72) reacts at about the same rate as its tetramethyl analogue (18) k_{rel} = 0.70) despite the fact that the πIp of the latter is 0.47 eV less. We do not, at this time, know the reasons for this equality in rates, but it may well be the result of a fortuitous balance between the increase in reactivity of (18) as a result of its lower πIp and an opposing "steric effect" of the methyl groups. We do note however, that there is little difference between the ratio of relative reactivities for the bicyclic ether (16) and the *cis*-diester (14) (k_{rel} = 0.70) in keeping with the similarity of their π Ip values (9.50 eV *vs* 9.25 eV, respectively). By comparison, the normally reactive anhydride (12) and corresponding imide (15) undergo little if any nitrene addition in competition with cyclohexene. That the latter is overwhelmingly faster is undoubtedly a reflection of its much lower π-ionisation potential [Δ Ip = 0.88 eV for (12) and 0.50 eV for (15)] and lends support to the qualitative conclusion from our previous study[3] that a reasonable correlation exists between reactivity and π-ionisation potential for the reactions of cyclic olefins with nitrenes. Based on the present results and those from our study with unsaturated cyclic sulphones, there seems little doubt that olefins with a πIp greater than *ca* 9.50 eV do not react with carboethoxynitrene, whilst the more reactive phthalimidonitrene will add to those olefins with values of up to 10 eV. These observations are consistent with the order of reactivity found for the Diels-Alder reactions of norbornene and of *endo*-norbornylene-2,3-dicarboxylic anhydride (21; X=CH_2) and its *exo*-isomer with phencyclone[42]. It was shown that the reactivity decreases in the order: norbornene (πIp = 8.97 eV) > *exo*-anhydride (π Ip = 9.61 eV) > *endo*-anhydride (π Ip = 9.85 eV) which correlates with the increase in the values of their first ionisation potentials. A similar trend is also found[47] between the kinetic data for the reactions of 3,6-di(2'-pyridyl)-*S*-tetrazine with a series of 2- and 9-substituted octahydrodimethanonaphthalenes, and their π-ionisation potentials.

We also briefly examined the behaviour of the present bicyclic olefins towards epoxidation but the results proved less instructive largely because normal epoxidising reagents show little discriminatory power in their reactions with double bonds. The only compound that could not be oxidised by any of the reagents tried was the cyclobutene anhydride (11). This compound, with its exceptionally high π Ip value of 10.49 eV, was inert to *m*-chloroperoxybenzoic acid (*m*-CPBA) in boiling ethyl acetate and also to t-butyl hydroperoxide/$Mo(CO)_6$[48] in boiling benzene, whilst treatment with peracetic or performic acids caused cleavage of the anhydride function. This complication did not occur with the six-membered ring analogue (12) (π Ip = 10.00 eV) which could be epoxidised in 32% yield by treatment with an anhydrous solution of peracetic acid in acetic acid at 40°C. In contrast to (11), epoxidation of the bridged anhydrides (21; X=CH_2) (πIp = 9.85 eV) and (21; X = CH_2CH_2) was easily accomplished with *m*-CPBA in boiling ethyl acetate, whereupon the products crystallised out on cooling in 46% and 33%, respectively. In the case of (21; X=O), treatment with performic acid produced the corresponding epoxy-diacid, which could be dehydrated back to the expected anhydride in 46% overall yield, either by heating with acetyl chloride or by vacuum sublimation.

EXPERIMENTAL

M.p.s are uncorrected. NMR spectra were recorded on a Varian EM360 (60 MHz) or HA100 (100 MHz) spectrometer using deuteriochloroform solutions (unless otherwise stated) of the compounds and tetramethylsilane as the internal standard; coupling constants are given in hertz with the following abbreviations for splitting patterns: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. IR spectra were recorded on a Perkin-Elmer 157G grating spectrophotometer. Mass spectra and accurate mass measurements were obtained with an AEI MS902 double focussing instrument (70 eV) using a direct insertion probe. Preparative column chromatography on silica was carried out by the medium pressure technique[49] (<60 lb in^{-2}) using 1000 x 25 or 1000 x 25 mm columns packed with Merck Kieselgel 60. For chromatography on alumina, material from Laporte Industries (Grade H, 100/200 mesh) deactivated to Grade III was used, with gravity elution. High performance liquid chromatography (h.p.l.c.) was carried out on a 25 x 0.5 cm column packed with Spherisorb S5Y using an ultraviolet detector (254 nm). All photolyses were carried out by irradiation through quartz with a water-cooled 125W or 400W medium pressure Hg lamp (Applied Photophysics); the course of reactions was monitored by t.l.c. and the visible evolution of nitrogen gas.

Ethyl *p*-nitrobenzenesulphonoxycarbamate (Lwowski's reagent) was prepared by the method of Lwowski and Maricich[40] as buff-coloured crystals (56%) from benzene, m.p. 115-116°C (lit.,[40] 116.4-116.8°C). Ethyl azidoformate was obtained in 85% yield according to the procedure of Lwowski and Mattingly,[50] and after distillation (n_D^{15} 1.4187) was stored in the dark at -30°C. *N*-Aminophthalimide was prepared as described by Drew and Hatt,[51] from phthalimide and hydrazine hydrate. The crude product was recrystallised from aqueous ethanol to give colourless needles (35-40%), m.p. 200-203°C (lit.,[51] 200-205°C). 1a-Acetyl-1a,6b-dihydro-1-phthalimidobenzofuro-[2,3-b]azirine (Jones' *N*-phthalimidoaziridine) was prepared from *N*-aminophthalimide and 2-acetyl-benzofuran as described by Jones[41] and obtained as pale-yellow prisms (79%) after trituration with ice-cold benzene (m.p. 134-135°C, lit., [41] 136-140°).

The following starting olefins were prepared by literature routes: 5-oxabicyclo[2.2.0]hex-2-en-6-one,[12] *N*-methyl-cis-1,2,3,6-tetrahydrophthalimide,[52] *cis*-8-oxabicyclo[4.3.0]non-3-ene,[10] 7,7,9,9-tetramethyl- *cis*-8-oxabicyclo[4.3.0]non-3-ene,[53] *endo*-3,5-dioxo-4-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene (*endo*-norbornylene-5,6-dicarboxylic anhydride),[54] *endo*-3,5-dioxo-4-oxatricyclo[5.2.2.0^{2,6}]undec-8-ene,[54], *exo*-3,5-dioxo-4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene.[55]

cis-Dimethyl 1,2,3,6-tetrahydrophthalate. - A solution of *cis*-1,2,3,6-tetrahydrophthalic anhydride (Aldrich) (10.0g) in absolute methanol (150 ml) containing 5 drops of conc. sulphuric acid was boiled under reflux for 6 h. The solvent was then evaporated off to leave a colourless oil which was washed free of acid by dissolution in ether and washing with saturated aqueous sodium bicarbonate. Drying and evaporation gave a colourless oil which was distilled to give *cis*-dimethyl 1,2,3,6-tetrahydrophthalate (7.80 g), b.p. 80-84°C at 0.05 mmHg (lit., [56] 110-111°C at 1 mmHg).

7,7-Dimethyl-*cis*-8-oxabicyclo[4.3.0]non-3-ene. - A solution of *cis*-6-hydroxymethyl-3-cyclohexene-1-carboxylic acid γ-lactone[57] (4.95 g, 35.8 mmol) in dry ether was added dropwise to a rapidly stirred solution of methylmagnesium iodide (from 3.26 g Mg and 19.3 g methyl iodide) (0.136 mol) in dry ether. The mixture was boiled under reflux for 1 h, cooled to 0°C, and hydrolysed with aqueous ammonium chloride (10% w/v). Extraction with ether, drying and evaporation gave a colourless solid (5.32 g) which was recrystallised from petroleum to give 3.56g of 2-(6'-hydroxymethylcyclohex-3'-enyl)propan-2-ol, m.p. 63-66°C (Found: C, 70.6; H, 10.5. $C_{10}H_{18}O_2$ requires C, 70.6; H, 10.6%), δ 1.21 (s, 3H), 1.32 (s, 3H), 1.54-2.63 (m, 6H), 3.08-4.0 (m, 2H), 5.10 (br.s, 2H; absent after D_2O shake) and 5.55 (br.s, 2H). The above diol (3.4 g) was heated at 150-160° for *ca.*10 min with a catalytic amount of *p*-toluenesulphonic acid. After cooling to room temperature, the oily product was dissolved in ether, washed with water and dried. Removal of the ether gave a yellow oil (2.7 g) which was distilled (bulb-to-bulb) at 100°C and 12 mmHg to give 7,7-dimethyl-*cis*-8-oxabicyclo[4.3.0]non-3-ene (2.34 g; 77%), δ1.06 (s, 3H), 1.14 (s, 3H), 1.75-2.60 (m, 6H), 3.40 (dd, J 8 and 5 Hz, 2H), 3.77 (dd, 8 and 6 Hz, 2H) and 5.68 (br. s, 2H).

cis-8-Thiabicyclo[4.3.0]non-3-ene. - A solution of *cis*-4,5-di(*p*-toluene sulphonoxymethyl)cyclohexene[58] (27.7 g, 61.6 mmol) and sodium sulphide nonahydrate (46.2 g, 190 mmol) in ethanol (160 ml) and water (160 ml) was heated under reflux for 12 h. After removal of the ethanol under reduced pressure, the residue was extracted with dichloromethane (3 x 200 ml). Drying and evaporation gave *cis*-8-thiabicyclo[4.3.0]non-3-ene (5.78 g, 67%) as a colourless oil, b.p. 83-84°C at 0.6 mmHg (Found: C, 68.7; H, 8.6. $C_8H_{12}S$ requires C, 68.5; H, 8.5%), δ2.12 (br.m, 4H), 2.28-2.50 (m, 2H), 2.50-2.78 (m, 2H), 2.78-3.02 (m, 2H) and 5.58 (t, 2H), m/z 140 (100%, M^+).

Reactions of *N*-phthalimidonitrene

(i) with 5-oxabicyclo[2.2.0]hex-2-en-6-one (8). To a stirred suspension of freshly prepared (8) (1.50 g; 15 mmol) and finely ground *N*-aminophthalimide (2.43 g; 15 mmol) in dry dichloromethane (45 ml) was added lead tetra-acetate (6.65 g; 15 mmol) in portions over a period of 20 min at room temperature. After a further 40 min the mixture was filtered, the solid was washed with dichloromethane, and the combined filtrate and washings were then washed with water, dried and evaporated to dryness. The residue was leached with hot benzene, and the leachings cooled to give 3-phthalimido-3-aza-6-oxatricyclo[$3.2.0.0^{2,4}$]heptan-7-one (0.41 g; 10%) as buff-coloured needles from carbon tetrachloride, m.p. 174–175°C (decomp) (Found: C, 60.5; H, 3.1; N, 10.8. $C_{13}H_8N_2O_4$ requires C, 60.9; H. 3.2; N, 10.9%), ν_{max} 1820, 1785, 1715, 1280, 1145, 1088, 960, 905, 862, 755 and 710 cm^{-1}, δ 3.85-4.10 (m, 3H), 4.83 (m, 1H) and 7.78 (m, 4H); m/z 256 (2%, M^+), 212 (58%) and 104 (100).

(ii) with *cis*-1,2,3,6-tetrahydrophthalic anhydride (12). A mixture of (12) (3.0 g, 19.7 mmol) and *N*-aminophthalimide (1.00 g, 6.2 mmol) was reacted with lead tetra-acetate (2.43 g, 5.53 mmol) in dry dichloromethane (30 ml). Following the usual work-up, crystallisation of the crude reaction mixture from chloroform gave 8,10-dioxo-4-phthalimido-4-aza-9-oxatricyclo[$5.3.0.0^{3,5}$]decane (0.23 g, 13%) as pale-yellow granules, m.p. 230°C (decomp), (Found: C, 61.3; H, 3.8; N, 8.8. $C_{16}H_{12}N_2O_5$ requires C, 61.5; H, 3.8; N, 9.0%), ν_{max} 1840, 1770, 1710, 940, 890, 710 and 705 cm^{-1}, δ(d_6-DMSO) 2.97 (br. s, 2H), 3.34 (br. m, 6H) and 7.74 (s, 4H); m/z 312 (45%, M^+) and 104 (100).

(iii) with *cis*-dimethyl 1,2,3,6-tetrahydrophthalate (14). A mixture of (14) (0.653 g, 3.29 mmol) and *N*-aminophthalimide (0.176 g, 1.08 mmol) was reacted with lead tetra-acetate (0.443 g, 1.0 mmol) in dry dichloromethane (10 ml). H.p.l.c. analysis of the reaction mixture showed the presence of *cis*-dimethyl 7-phthalimido-7-azabicyclo[4.1.0]heptane-3,4-dicarboxylate as *syn*- and *anti*-isomers in 2.7 and 17.0% yield, respectively.

In a subsequent preparative experiment, work-up in the usual way followed by chromatography [silica; petroleum-acetone (3:1)] gave pale yellow needles assigned to the *syn*-isomer, m.p. 150-155°C, δ 2.10-2.38 (m, 2H), 2.70–3.15 (m, 6H), 3.65 (s, 6H) and 7.68 (m, 4H); m/z 358 (25%, M^+), 327 (27), 299 (62), 212 (40), 197 (37), 152 (100), 137 (58), and 104 (92), and the *anti*-isomer, m.p. 163-166°C (Found: C, 60.2; H, 5.0; N, 7.7. $C_{18}H_{18}N_2O_6$ requires C, 60.3; H, 5.0; N, 7.8%, δ 2.40 (m, 4H), 2.88 (m, 4H), 3.62 (s, 6H), 7.66 (m, 4H), m/z 358 (19%, M^+) and 104 (100).

(iv) with *N*-methyl-*cis*-1,2,3,6-tetrahydrophthalimide (15). A mixture of (15) (0.691 g, 4.2 mmol) and *N*-aminophthalimide (0.214 g, 1.3 mmol) was reacted with lead tetra-acetate (0.541 g, 1.22 mmol) in dry dichloromethane (15 ml). After work-up in the usual way, the mixture was examined by h.p.l.c, which showed the presence of 8,10-dioxo-9-methyl-4-phthalimido-4,9-diazatricyclo[$5.3.0.0^{3,5}$]decane (28%) as a mixture of *syn*- and *anti*-isomers. Chromatography (silica, dichloromethane) gave one isomer as pale yellow leaflets from ethanol, m.p. 232-234°C (Found: C, 62.8; H, 4.6; N, 12.9. $C_{17}H_{15}N_3O_4$ requires C, 62.8; H, 4.6; N, 12.9%), ν_{max} 1767, 1715, 1690, 1175, 1137, 1055, 893, 782, 708, 702 cm^{-1}, δ 1.78-2.22 (m, 2H), 2.68-3.18 (m), 2.90 (br. s), 2.96 (s) (total 9H) and 7.68 (m, 4H); m/z 325 (89%, M^+) and 104 (100), and the other as cream needles from ethanol, m.p. 206-208°C (Found: C, 62.6; H, 4.7; N, 12.7. $C_{17}H_{15}N_3O_4$ requires C, 62.8; H, 4.6 and N, 12.9%), ν_{max} 1770 (br), 1710, 1690, 1315, 1130, 955, 886, 875, 782, 709 and 702 cm^{-1}, δ 1.98-2.28 (m, 2H), 2.78-3.18 (m), 2.99 (s) (total 9H) and 7.68 (m, 4H); m/z 325 (20%, M^+) and 104 (100).

(v) with *cis*-8-oxabicyclo[4.3.0]non-3-ene (16). A mixture of (16) (0.30 g, 2.4 mmol) and *N*-aminophthalimide (0.131 g, 0.81 mmol) was reacted with lead tetra-acetate (0.354 g, 0.80 mmol) in dry dichloromethane (10 ml). After work-up in the usual way, analysis of the crude product by h.p.l.c. showed it to contain 4-phthalimido-9-oxa-4-azatricyclo[$5.3.0.0^{3,5}$]decane (24%) which could be isolated by column chromatography (silica, dichloromethane) as yellow crystals, m.p. 163-166°C (Found: C, 67.4; H, 5.5; N, 9.9. $C_{16}H_{16}N_2O_3$ requires C, 67.6; H, 5.6; N, 9.8%), δ 1.63-2.18 (m, 6H), 2.80 (m, 2H), 3.38-3.97 (m, 4H) and 7.70 (m, 4H); m/z 284 (51%, M^+), 202 (62), 188 (43), 148 (35) and 104 (100).

A solution of (16) (1.01 g, 8.18 mmol) and Jones' aziridine (24) (0.86 g, 2.69 mmol) in anhydrous benzene (15 ml) was boiled under reflux for 5 h. Evaporation of the solvent gave a brown residue which was found to contain 4-phthalimido-9-oxa-4-azatricyclo[$5.3.0.0^{3,5}$]decane (18.3%) by h.p.l.c. analysis (3% ethanol-hexane).

(vi) with 7,7-dimethyl-*cis*-8-oxabicyclo[4.3.0]non-3-ene (17). A mixture of (17) (1.34 g, 10.47 mmol) and *N*-aminophthalimide (0.59 g, 3.65 mmol) was reacted with lead tetra-acetate (1.55 g, 3.50 mmol) in dry dichloromethane (15 ml). Work-up in the usual way, followed by column chromatography [silica; petroleum-acetone (10:1)] gave a yellow solid which was recrystallised from ethanol to give 8,8-dimethyl-4-phthalimido-9-oxa-4-azatricyclo[$5.3.0.0^{3,5}$]decane (0.19 g, 18%) as yellow crystals, m.p. 129–132°C. (Found: C, 68.9; H, 6.4; N, 9.0. $C_{18}H_{20}N_2O_3$ requires C, 69.2; H, 6.4; N, 9.0%), δ 1.17 and 1.18 (total 6H), 1.55-3.0 (m, 8H), 3.42 (br. t, J 7 Hz, 1H), 3.92 (br. t, J 7 Hz, 1H) and 7.68 (4H); m/z 312 (22%, M^+) and 104 (100).

(vii) with 7,7,9,9-tetramethyl-*cis*-8-oxabicyclo[4.3.0]non-3-ene (18). A mixture of (18) (1.805 g, 0.01 mol) and *N*-aminophthalimide (1.623 g, 0.01 mol) was reacted with lead tetra-acetate (4.43 g, 0.01 mol) in dry dichloromethane (45 ml). After work-up in the usual way, the residue was leached with hot dichloromethane and the combined leachings chromatographed [alumina; petroleum-dichloromethane (1:1)] to give 4-phthalimido-8,8,10,10-tetramethyl-9-oxa-4-azatricyclo[$5.3.0.0^{3,5}$]decane (0.40 g, 12%) as yellow needles from ethanol, m.p. 148–150°C (Found: C, 70.7; H, 7.1; N, 8.2. $C_{20}H_{24}N_2O_3$ requires C, 70.6; H, 7.1 and N, 8.2%), ν_{max} ($CHCl_3$) 1765, 1710, 1375, 968, 700 cm^{-1}, δ 1.18 and 1.22 (total 12H), 1.80-2.65 (m, 6H), 2.87 (br. s, 2H) and 7.70 (m, 4H).

In a subsequent experiment use of a 3 molar excess of (18) gave a yield of 15.9% by h.p.l.c. analysis; in the presence of an equivalent amount of succinic anhydride it was 15.3%.

(viii) with *cis*-8-thiabicyclo[4.3.0]non-3-ene (20). A mixture of (20) (1.40 g), 10.0 mmol) and *N*-aminophthalimide (1.62 g, 10 mmol) was reacted with lead tetra-acetate (4.49 g, 10.0 mmol) in dry dichloromethane (25 ml). After work-up in the usual way, column chromatography (basic alumina; petroleum) gave recovered starting material (1.20 g), followed by a pale-yellow oil, (0.445 g), identified by m.s.-g.l.c. analysis (150°C, 5% SE 30) as a *ca.*1:1 mixture of *syn* - and *anti-cis* -8-thiabicyclo[4.3.0]non-3-ene 8-oxide,(26) m/z 156 (87%, M^+), 139 (53), 107 (69), 105 (38), 93 (98), 92 (60), 91 (100), 85 (64), 79 (90), 77 (93) and 60 (78).

(ix) with norbornene. A mixture of norbornene (1.86 g, 20 mmol) and *N*-aminophthalimide (2.43 g, 15 mmol) was reacted with lead tetra-acetate (6.65g, 15 mmol) in dry dichloromethane (45 ml). After work-up in the usual way, the residue was leached several times with hot ether and the combined leachings chromatographed [silica; dichloromethane-ether (10:1) to give a yellow oil (0.93 g, 25%) which gradually crystallised. Recrystallisation from cyclohexane afforded 3-phthalimido-3-azatricyclo[3.2.1.$0^{2,4}$]octane as a yellow crystalline solid, m.p. 122-125°C (Found C, 70.4; H, 5.5; N, 11.0%), ν_{max} 1765, 1710, 1287, 1182, 1137, 1045, 990, 897, 828, 796 and 712 cm^{-1}, δ0.75 (br. d, J 10 Hz, 1H), 1.13-1.74 (m, 5H), 2.74 (s, 2H), 2.78 (s, 2H) and 7.66 (m, 4H); m/z 254 (25%, M^+), 226 (58), 225 (100), 147 (60) and 104 (32).

Competition Studies. - The competition studies were performed by allowing an equimolar mixture of cyclohexene and other alkenes to complete for a limiting amount of phthalimidonitrene generated by oxidation of *N*-aminophthalimide with lead tetra-acetate in dichloromethane. After the reactions were complete (*ca.*15-20 min), the crude product mixture was analysed for product by h.p.l.c. using authentic compounds as internal standards. The following reactivity ratios were obtained: cyclohexene vs (16) (1:0.83); cyclohexene vs (18) (1:0.84); (16) vs (18) (1:0.96); cyclohexene vs (14),(16) and (18) (1:0.70::0.72:0.70).

Formation of *N*-carboethoxyaziridines

(a) from *endo*-3,5-dioxo-4-oxatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (21; X=CH_2).

(i) Photochemical reaction with ethyl azidoformate

A mixture of (21; X=CH_2) (0.50 g, 3.0 mmol) and ethyl azidoformate (1.0 g, 8.7 mmol) was irradiated for 18 h. Ether (10 ml) was added to the oily solid and trituration gave a white solid. This was filtered off and washed with ether to give 3,5-dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.1.$0^{2,6}0^{8,10}$]undecane (0.49 g, 64%) as colourless crystals, m.p. 184-185°C. (Found: C, 57.4; H, 5.3; N, 5.4. $C_{12}H_{13}NO_5$ requires C, 57.4; H, 5.2; N, 5.6%); ν_{max} 1861, 1790, 1714, 1293, 1270, 1224, 1192, 1087, 1022, 950, 916, 793 and 721 cm^{-1}; δ 4.11 (2H, q, J 7 Hz), 3.44 (2H, m), 3.13 (2H, m), 2.86 (2H, s), 1.85 and 1.18 (2H, AB pattern, J 11 Hz) and 1.25 (3H, t, J 7 Hz); m/z 251 (2.4%, M^+), 223 (10), 206 (6), 179 (25), 153 (52), 152 (83), 127 (45), 108 (46), 106 (38), 96 (60) and 79 (100).

(b) from *endo*-3,5-dioxo-4-oxatricyclo[5.2.2.$0^{2,6}$]undec-8-ene (21; X=CH_2CH_2)

(i) Photochemical reaction with ethyl azidoformate.

A mixture of (21; X=CH_2CH_2) (0.50 g, 2.81 mmol) and ethyl azidoformate (1.0 g, 8.7 mmol) was irradiated for 18 h. Ether (10 ml) was added to the resulting yellow oil and the product filtered off and washed with ether. Vacuum sublimation at 10^{-3} mmHg and 150°C gave 3,5-dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodecane (0.17 g, 23%) as colourless crystals, m.p. 208-209°C. (Found: C, 58.6; H, 5.7; N, 5.2. $C_{13}H_{15}NO_5$ requires C, 58.9; H, 5.7; N, 5.3%); ν_{max} 1848, 1773, 1725, 1408, 1287, 1212, 1100, 1083, 1020, 948, 913 and 784 cm^{-1}; δ 4.12 (2H, q, J 7 Hz), 3.12 (2H, 2s), 2.84 (2H, m), 2.78 (2H, s), 1.90 and 1.27 (4H, A_2B_2 pattern, J 8 Hz) and 1.24 (3H, t, J 7 Hz); m/z 265 (11%, M^+), 220 (9), 193 (30), 165 (37), 120 (56), 99 (27), 95 (40), 93 (74) and 80 (100).

Addition of ether (10 ml) to the resulting yellow oil from the corresponding irradiation with methyl azidoformate gave a colourless solid which was recrystallised fromchloroform/ether (1:3) to give 3,5-dioxo-9-methoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodecane (0.10 g, 15%) as colourless needles, m.p. 221-223°C. (Found: M^+ 251.080686. $C_{12}H_{13}NO_5$ requires 251.079365); ν_{max} 1840, 1765, 1710, 1444, 1292, 1209, 1148, 1082, 1010, 942, 909, 825 and 783 cm^{-1}; δ($CDCl_3$/CD_3COCD_3, 3:1) 3.68 (3H, s), 3.25 (2H, s), 2.81 (4H, s) and 1.89 and 1.33 (4H, A_2B_2 pattern, J 8 Hz); m/z 251 (24%, M^+), 223 (3), 220 (8), 179 (45) and 153 (100).

(ii) Thermal reaction with ethyl azidoformate

A solution of (21; X=CH_2CH_2) (0.10 g, 0.56 mmol) and ethyl azidoformate (0.07 g, 0.61 mmol) in dry carbon tetrachloride (10 ml) was heated under reflux for 40 h. Evaporation gave a brown solid whose NMR and TLC (alumina, Et_2O) showed the presence of azide byproducts, the starting anhydride (86 mg) and 3,5-dioxo-9-ethoxycarbonyl-4-oxa-9-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodecane (21 mg, 14%). [Yields estimated from NMR].

(iii) Attempted homogeneous reaction with carboethoxynitrene from α-elimination

To a solution of (21; X=CH_2CH_2) (0.50 g, 2.81 mmol) and ethyl *p*-nitrobenzenesulphonoxycarbamate (0.86 g, 2.96 mmol) in dry methylene chloride (10 ml), was added a solution of triethylamine (0.40 g, 3.96 mmol) in dry methylene chloride (5 ml) over 5 min. After stirring for 3 h the solution was washed with water (2 x 10 ml), dried and evaporated. NMR and TLC (alumina, Et_2O) of the residue showed only nitrene byproducts and the unreacted starting anhydride with none of the expected aziridine.

(c) from *exo*-3,5-dioxo-4,10-dioxatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (21; X=O)

(i) Photochemical reaction with ethyl azidoformate

A mixture of (21; X=O) (0.50 g, 3.01 mmol) and ethyl azidoformate (2.0 g, 17.4 mmol) was irradiated for 72 h. Addition of ether (10 ml) gave a white solid which was filtered off and washed with ether. Vacuum sublimation at 10^{-3} mmHg and 140°C gave 3,5-dioxo-9-ethoxycarbonyl-4,11-dioxa-9-azatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]undecane (0.20 g, 26%) as a white powder, m.p. 178-179°C. (Found: C, 52.0; H, 4.4; N, 5.4. $C_{11}H_{11}NO_6$ requires C, 52.2; H, 4.4; N, 5.5%); ν_{max} 1868, 1788, 1740, 1327, 1300, 1223, 1188, 1090, 1025, 942, 927, 908, 840, 820, 799, 740 and 690 cm^{-1}; δ 5.05 (2H, s), 4.13 (2H, q, J 7 Hz), 3.36 (2H, s), 2.91 (2H, s) and 1.24 (3H, t, J 7 Hz); m/z 253 (1%, M^+), 208 (9), 180 (5), 155(100), 111 (31) and 83 (91)

(ii) Thermal reaction with ethyl azidoformate

A solution of (21; X=O) (0.50 g, 3.01 mmol) and ethyl azidoformate (0.40 g, 3.48 mmol) in dry carbon tetrachloride (10 ml) was heated under reflux for 18 h. Evaporation gave a brown oil

(0.61 g) whose NMR showed the presence of azide byproducts and maleic anhydride from the retro Diels-Alder reaction of the starting anhydride. There was none of the starting anhydride or of the expected aziridine.

(iii) Attempted homogeneous reaction with carboethoxynitrene from α-elimination
To a solution of (21; X=O) (0.50 g, 3.01 mmol) and ethyl *p*-nitrobenzenesulphonoxycarbamate (0.92 g, 3.17 mmol) in dry methylene chloride (20 ml), was added a solution of triethylamine (0.34 g, 3.37 mmol) in dry methylene chloride (10 ml) over 10 min. After stirring for 8 h the solution was washed with water (3 x 50 ml), dried and evaporated to give a yellow oil (0.72 g). The NMR showed the presence of the starting anhydride, furan and maleic anhydride from the retro Diels-Alder reaction and nitrene byproducts. There was none of the expected aziridine.

(d) from norbornene
To a stirred solution of norbornene (0.94 g; 10 mmol) and ethyl *p*-nitrobenzenesulphonoxycarbamate (2.90 g, 10 mmol) in dry dichloromethane (45 ml) was added dropwise a solution of triethylamine (1.05g, 10.5 mmol) in dry dichloromethane (10 ml). After 3 h, the solution was washed with water, dried and evaporated to leave a pale yellow oil (1.24 g). Chromatography (alumina; dichloromethane) gave 3-ethoxycarbonyl-3-azatricyclo[3.2.1.$0^{2,4}$]octane (0.35 g, 20%). as a pale yellow oil, b.p. 75-80°C at 1 mmHg (lit.[59] 99-100°C at 2.4 mmHg); ν_{max} 1715, 1375, 1300, 1265, 1185, 1097, 1032, 832 and 790 cm^{-1}; δ1.75 (d, J 10 Hz, 1H), 1.26 (t, J 7 Hz) and 1.08-1.58 (m) (total 8H), 2.50 (br. s, 2H), 2.61 (s, 2H) and 4.12 (q, J=7 Hz, 2H); m/z 181 (27%, M^+), 153 (60), 152 (100), 108 (37) and 81 (80).

Epoxidation
(i) of 7,9-dioxo-8-oxabicyclo[4.3.0]non-3-ene (12).
The method used was based on that of Gill and Munro[60]. A solution of peracetic acid in acetic acid was prepared by stirring a mixture of acetic anhydride (12.9 g, 126 mmol) with 30% hydrogen peroxide solution (2.6 ml, 23.4 mmol) at 40°C for 4 h. (12) (2.0 g, 13.2 mmol) was then added and the solution stirred at room temperature for 18 h. The solid was filtered off and recrystallised from ethyl acetate to give 8,10-dioxo-4,9-dioxatricyclo[5.3.0.$0^{3,5}$]decane (0.70 g, 32%) as colourless needles, m.p. 205-206°C (lit.[60] 204-205°C).

(ii) of*endo* -3,5-dioxo-4-oxatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (21; $X=CH_2$).
A solution of (21; $X=CH_2$) (1.0 g, 6.1 mmol) and *m*-chloroperoxybenzoic acid ('85%', 2.5 g, contains 12.3 mmol peracid) in dry ethyl acetate (25 ml) was heated under reflux for 8 h. The solution was cooled and on standing the product crystallised out. It was filtered off and recrystallised from pet. ether/acetone (1:1) to give 3,5-dioxo-4,9-dioxatetracyclo-[5.3.1.$0^{2,6}$.$0^{8,10}$]undecane (0.50 g, 46%) as colourless flakes, m.p. 235-237°C (lit.[61] 233-235°C).

(iii) of *endo*-3,5-dioxo-4-oxatricyclo[5.2.2.$0^{2,6}$]undec-8-ene (21; $X=CH_2CH_2$).
A solution of (21; $X=CH_2CH_2$) (1.0 g, 5.6 mmol) and *m*-chloroperoxybenzoic acid ('85%', 2.5 g, contains 12.3 mmol peracid) in dry ethyl acetate (25 ml) was heated under reflux for 15 h. On cooling at 0°C for 12 h the product crystallised out and was filtered off to give 3,5-dioxo-4,9-dioxatetracyclo[5.3.2.$0^{2,6}$.$0^{8,10}$]dodecane (0.36 g, 33%) as colourless crystals, m.p. 209-211°C (lit.[62] 207-208°C).

(iv) of *exo*-3,5-dioxo-4,10-dioxatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (21; X=O).
A solution of (21; X=O) (1.0 g, 6.0 mmol) in formic acid (10 ml) containing 30% hydrogen peroxide solution (4.0 ml, 36 mmol) was stirred at room temperature for 64 h. The solution was evaporated to give the epoxy diacid as a white solid (1.19 g), m.p. 182-184°C. This was then heated with acetyl chloride (10 ml) under reflux for 12 h. The residue on evaporation was a brown solid (0.83 g) which was sublimed onto a cold finger at 220°C and 0.03 mmHg to give 3,5-dioxo-4,9,11-trioxatetracyclo[5.3.1.$0^{2,6}$.$0^{8,10}$]undecane (0.66 g, 72%) as colourless crystals, m.p. 252-253°C (lit.[63] 247-253°C). (Found: C, 52.5; H, 3.4. $C_8H_6O_5$ requires C, 52.8; H, 3.3%)

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