Photoinduced [2 + 2] cycloadditions (the Paterno–Büchi reaction) of 1*H*-1-acetylindole-2,3-dione with alkenes

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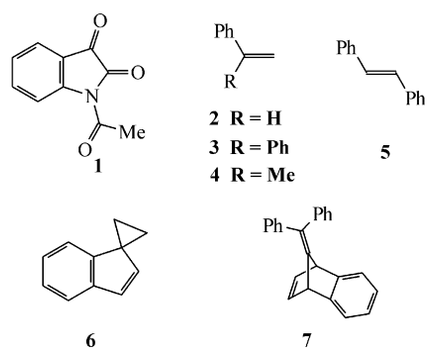
Photoinduced cycloadditions of 1-acetylisatin (**1**) with alkenes **2**–**7** give spiroxetanes **8**–**21** respectively in moderate to high yields, displaying a typical triplet *n*–π* reactivity for **1**. The regioselectivity and diastereoselectivity of the reactions depend on the reaction mechanism. In reactions with alkenes of high oxidation potential (**2** and **4**) where single-electron transfer (SET) processes with triplet excited **1** are not involved, the regioselectivity can be rationalized by consideration of frontier molecular orbital interactions of the two addends, and the Salem–Rowland rules for diradical intersystem crossing explains the diastereoselectivity. For the more electron-rich alkenes, *e.g.* **5**–**7**, SET processes with ^{3}**1*** and ion-radical pair formation are energetically feasible, and the cycloaddition regioselectivity is dependent on charge and spin-density distribution in the ion-radicals and the diastereoselectivity is also decided by ion-radical pair collapse.

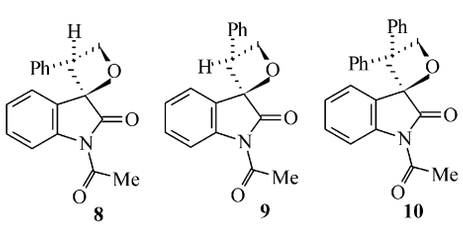
1*H*-Indole-2,3-dione (isatin) derivatives have various biological activities.[1] They are also basic structural units and important synthetic precursors of many naturally occurring alkaloids.[2] However, photochemical reactions of isatin derivatives have not yet been much investigated,[3] even less so their photoreactions *via* single-electron transfer (SET) mechanisms[3] despite their triplet excited state (T_1 state) having typical n–π* reactivity[4] and being a strong electron acceptor due to a combination of high electron affinity and a rather high triplet energy. (As an example, 1-acetylisatin **1** has a triplet energy of ≈64 kcal mol^{-1}† and a reduction potential of −0.75 V *vs.* saturated calomel electrode (SCE). The excited-state reduction potential of **1** is therefore ≈2 V *vs.* SCE.) We report here an investigation on photoinduced [2 + 2] cycloadditions (the Paterno–Büchi reaction[5]) of 1-acetylisatin **1** with alkenes **2**–**7**. These reactions provide an efficient access to spiro(3*H*-indole-3,2′-oxetane) derivatives.

Alkenes **2**–**7** could all be viewed as styrene derivatives. By introducing different α- and β-substituents, the steric environment around the C=C bond and the oxidation potential of the alkenes can be modified to facilitate scrutiny into the structural factors that affect the reaction regioselectivity and stereoselectivity, and the search for their mechanistic origins. In addition, it is found that photoinduced cycloadditions of **1** with all the alkenes **2**–**7** take place cleanly in high chemical yields and with high regioselectivity. These characteristics of the cycloadditions simplify the rationalization of the addition stereoselectivity which has currently drawn considerable interest in the investigation of the Paterno–Büchi reactions.[6]



Results

Photoinduced reactions of **1** with alkenes **2**–**7** respectively in benzene invariably take place at the C-3 carbonyl group of **1** and give the corresponding spiroxetane products **8**–**21** *via* [2 + 2] cycloaddition in moderate to high yield, reflecting a typical triplet n–π* reactivity of **1**. The reaction conditions and the product yields are listed in Table 1. In all cases except **3**, the products were obtained as mixtures of diastereoisomers. The diastereoisomeric ratios are determined by high-resolution ^{1}H NMR measurements of the crude product mixtures and the structures of the products were determined by their spectral data (IR, ^{1}H NMR, MS) and elemental analyses, and in some cases (products **8**, **11**, **13** and **19**) further established by X-ray crystallographic analysis (*vide infra*).



There are several common features in the spectral data of these spiroxetane products. In the IR spectra, the two asymmetric C–O–C stretching bands of the oxetane ring are at ≈980 and 1030 cm^{-1}.[7] In the mass spectrum, oxetane-ring metathesis yields the peak of the corresponding *o*-quinone methide fragments, from the *m*/*z*-value of which the regiochemistry in the spiroxetanes can be derived. At the same time, retrocycloaddition leads to the cation-radical peak for the starting **1**.

In the photoreactions of **1** with styrene **2** in benzene, the *syn*- (refers to the *syn*- relationship between the phenyl group from **2**

† 1 cal = 4.184 J.

Table 1 Photoinduced cycloaddition reactions of **1** with alkenes[a]

Alkene	Solvent	Irradiation time (*t*/h)	Conversion of **1** (%)	Products and yields[b,c] (%)
2	PhH	7	100	**8** and **9**, 96% (1.42 : 1)
2	MeCN	24		**8** : **9** = 2.57 : 1
3	PhH	16	100	**10**, 98%
3	MeCN			
4	PhH	14	100	**11** and **12**, 96% (1 : 1.64)
4	MeCN	24		**11** : **12** = 2.19 : 1
5	PhH	36	58	**13**, **14** and **15**, 56% (2.9 : 1 : 8.2)
5	MeCN	24	<1.5	**13** : **14** : **15** = 1 : 1.4 : 5
(*Z*)-**5**	PhH	24		**13** : **14** : **15** = 1.2 : 1 : 8
6	PhH	8	100	**16** and **17**, 90% (2.5 : 1)
7	PhH	18	100	**18**, **19**, **20** and **21**, 70% (1.2 : 4 : 2 : 1)
7	MeCN	60	100	**18**, **19**, **20** and **21**, 37% (1 : 6 : 20 : 10)

[a] Irradiation wavelength: $\lambda > 400$ nm. [b] Isolated yield based on consumed *N*-acetylisatin. [c] Determined by ^{1}H NMR (500 MHz or 300 MHz) measurement of the product mixture.

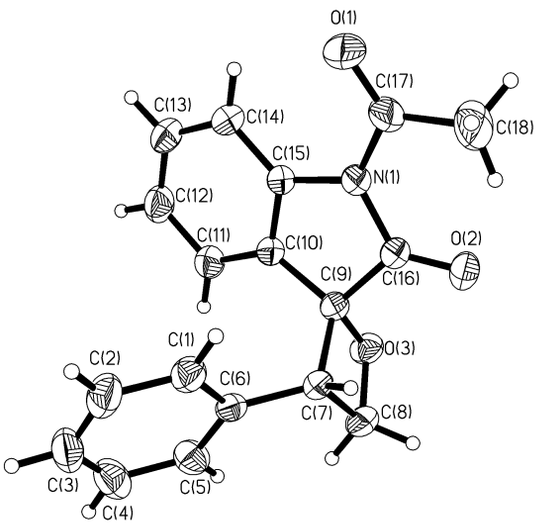


Fig. 1 X-Ray structure of **8**.

and the phenyl ring in **1**) and *anti*- spiroxetanes **8** and **9** were obtained as an inseparable mixture by chromatography on silica gel in a total yield of 96%. The *syn*/*anti* quotient is 1.42, in favor of the *syn* isomer, as determined by integration of the well separated olefinic-proton absorptions of **8** and **9** in the high-resolution ^{1}H NMR spectrum of the crude product mixture. Pure analytical samples of **8** and **9** were obtained by fractional crystallization of the crude products and an X-ray crystallographic analysis of the *syn* product **8** has been carried out (Fig. 1). The main differences in the ^{1}H NMR spectra of the two isomers are in the aromatic and the acetyl methyl absorptions. In the *syn* isomer, some of the protons in the two phenyl groups are in each other's shielding area and resonate at higher field than do the corresponding aromatic protons in the *anti* isomer. The protons of the acetyl methyl in the *anti* isomer are slightly shielded by the *anti*-phenyl ring and absorb at a higher field (δ 2.29) as compared with $\delta \approx 2.76$ for the same methyl in the *syn* isomer.

Irradiation of **1** with styrene under similar conditions in the polar solvent acetonitrile, on the other hand, further increases the preference of the formation of the *syn* product and resulted in a *syn*/*anti* quotient of 2.57.

Photolysis of **1** with 1,1-diphenylethylene **3** in benzene under the conditions mentioned above afforded product **10** in 98% yield. The two diastereotopic protons in the oxetane ring absorb at δ 5.53 and 6.08 respectively as a pair of doublets with a *J*-value of 6 Hz. It was further found that cycloaddition reaction between **1** and **3** could not take place in acetonitrile even after prolonged irradiation, and, in the ^{1}H NMR spectrum of the reaction mixture after evaporation of solvent and the alkene, signals of product **10** were not found.

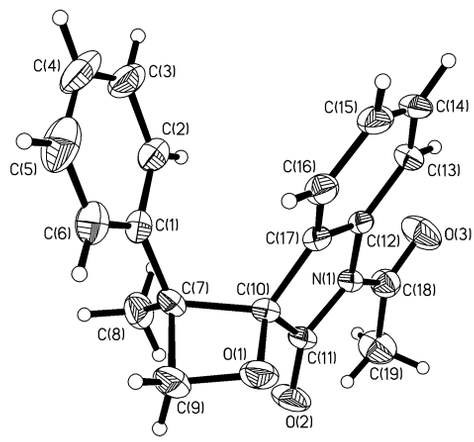
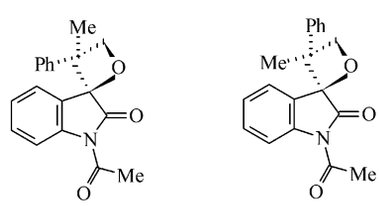


Fig. 2 X-Ray structure of **11**.

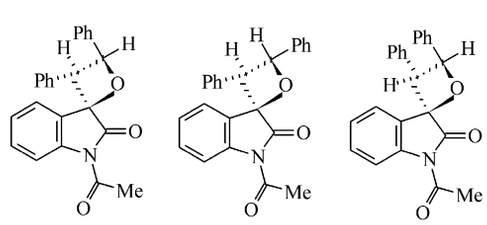
Similar irradiation of **1** with α-methylstyrene **4** in benzene gave the diastereoisomeric *syn*- and *anti*-spiroxetanes **11** and **12** in a ratio of 0.61 : 1 in 96% yield. Repeated crystallization of the



11 **12**

product mixture from ethyl acetate–petroleum spirit gave a pure analytical sample of **11**. An X-ray crystallographic analysis of this sample definitely confirmed the assigned structure (Fig. 2). Again, in the *anti* product, the acetyl methyl protons resonate at higher field (δ 2.12) than do those of the *syn* isomer ($\delta \approx 2.75$). In this case, photolysis of **1** with **4** in acetonitrile resulted in a much slower reaction and the product ratio was reversed (*syn*/*anti* = 2.19) compared with that in benzene (0.61).

In the photoreactions of **1** with (*E*)-stilbene **5**, three diastereoisomeric spiroxetane products **13**, **14** and **15** were formed.



13 **14** **15**

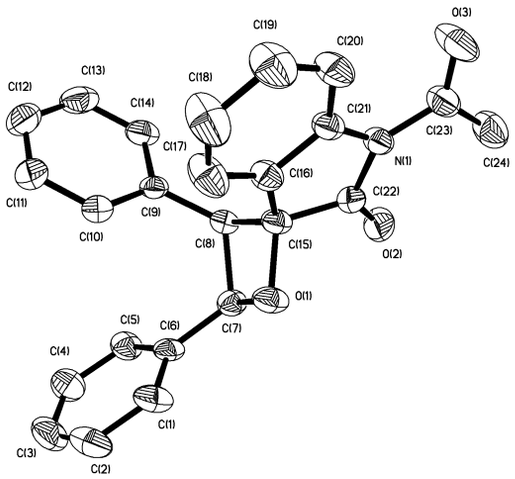


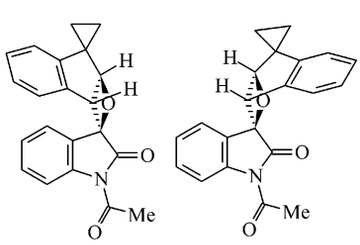
Fig. 3 X-Ray structure of **13**.

The product proportions determined from the high-resolution ^{1}H NMR spectrum of the crude product mixture were 2.9 : 1 : 8.2. Pure product **13** was obtained by fractional crystallization of the crude product mixture from ethyl acetate–petroleum spirit, and an X-ray crystallographic analysis of this sample unambiguously established its structure as the *syn*-/*cis*-isomer (Fig. 3). Compound **15** is a *trans* product with the 3-Ph group in the oxetane ring being *anti* to the isatin phenyl ring as judged from its ^{1}H NMR spectrum in which the acetyl methyl protons absorb at a field strength ≈0.4 ppm higher than in the *syn* product **13**, and the *syn*-methine proton (H-3 in **15**) also moves upfield to δ 4.61 from δ 5.05 in **13**, due to the shielding effect of the *syn*-C-2 phenyl. Similar ^{1}H NMR data analysis indicated that **14** is another *E* product, in which the 3-phenyl and 2-phenyl groups in the oxetane ring are *syn* and *anti* to the isatin framework, respectively.

Irradiation of **1** with (*E*)-stilbene in acetonitrile led to very sluggish reactions and, after 24 h irradiation, ^{1}H NMR measurement of the reaction mixture after evaporation of the solvent showed that the ratio of products (**13** + **14** + **15**) to unchanged **1** was ≈1 : 75 which corresponds to a ≈1.5% conversion of the starting material **1**. Photoinduced reactions of **1** with (*Z*)-stilbene were also investigated. Photolysis in benzene gave the same three products **13**, **14** and **15**. The relative amounts of products were **15** > **13** > **14**, the same as in the reactions of **1** with (*E*)-stilbene, but the product proportions were 8.0 : 1.2 : 1.

It was also found that *E*/*Z*-isomerizations of the starting alkenes took place during the cycloadditions of **1** with the (*E*)- and (*Z*)-stilbenes.

As another example of the photoinduced reactions of **1** with styrene derivatives, photocycloadditions of **1** with the spiro-[cyclopropane-1,1′-indene] **6** were further investigated. Two diastereomers - the *syn*-**16** and the *anti*-**17** - were formed in the



16 **17**

ratio 2.5 : 1 in a total yield of 90%. No other regioisomeric products were found in the reaction mixture after photolysis.

In relation to the styrene series **2**–**6**, we have also investigated the photocycloaddition of **1** to 9-diphenylmethylenebenzonorbornene **7** in benzene. This gave two pairs of diastereomers (**18**, **19**) and (**20**, **21**) in the proportions **18** : **19** : **20** : **21** = 4 : 1.2 : 2 : 1.

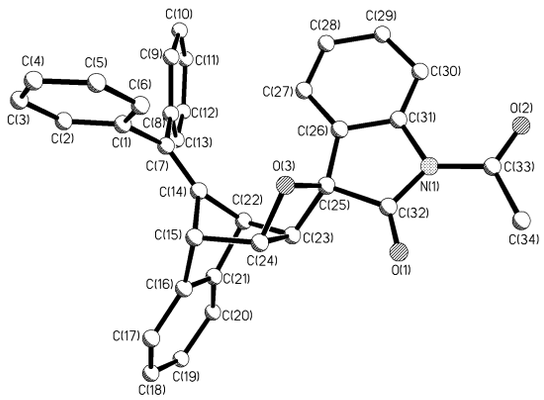
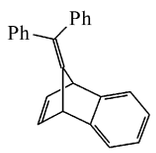
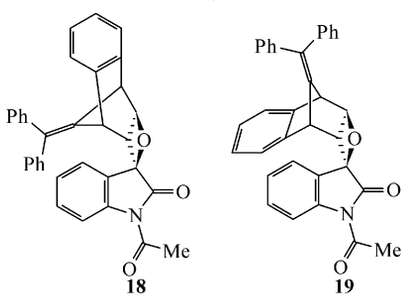


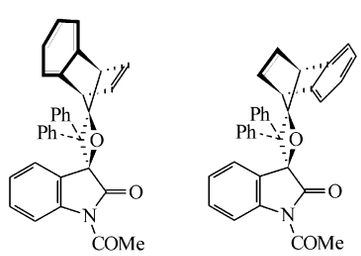
Fig. 4 X-Ray structure of **19**.



7



18 **19**



20 & 21

Compounds **18** and **19** were obtained as pure products by recrystallization of the crude product mixture. The structure of **19** was determined by X-ray crystallographic analysis to have the configuration shown in Fig. 4.[8] In products **20** and **21**, the reaction site is at the *exo*-cyclic C=C bond. The stereochemistry of these two products was not established.

Discussion

1. Regioselectivity in the cycloadditions

The prediction and rationalization of cycloaddition regioselectivity in view of the reaction mechanism has long been the research focus in the Paterno–Büchi reaction. The early arguments on the formation of the most stable 1,4-diradical intermediates[9] explained many experimental results but failed in some cases, especially when charge transfer interactions between the two addends play an obvious role in the reactions. In some of these cases, the intervention of exciplex intermediates with profound charge transfer character or even ion-radical pairs prior to the formation of 1,4-diradicals has been suggested to rationalize the observed regioselectivity[10] in the cycloadditions. This exciplex–1,4-diradical mechanistic picture is based on a diversity of experimental facts, ranging from the kinetic isotope effect,[11] correlation of the quenching rate con-

Table 2 Free-energy change for SET between ^{3}**1*** and alkenes **2**–**7**

Alkene	$E_{1/2}^{ox}$ (V *vs.* SCE)	Solvent	ΔG_{ET}[a] (kcal mol^{-1})
2	2.22[b]	PhH	13.3
2	2.22	MeCN	3.1
3	1.78[c]	PhH	3.1
3	1.78	MeCN	−7.0
4	2.15[d]	PhH	11.7
4	2.15	MeCN	1.5
5	1.50[e]	PhH	−3.4
5	1.50	MeCN	−13.5
(*Z*)-**5**	1.59[e]	PhH	−1.3
6	1.55[f]	PhH	−2.2
7	1.49[f]	PhH	−3.6
7	1.49	MeCN	−13.7

[a] Calculated by the Weller equation.[19] 1 cal = 4.184 J. [b] Ref. 20. [c] Ref. 21. [d] Ref. 22. [e] Ref. 23. [f] Measured by cyclic voltammetry, see Experimental section.

stants of the ketone triplet with the alkene ionization potentials (oxidation potentials),[10,12] as well as direct detection of ion-radicals by EPR[13] and transient absorption spectroscopic[14] measurements. Frontier molecular orbital (FMO) interaction considerations also meet with considerable success in this respect.[15]

Photoinduced cycloadditions of triplet n,π* carbonyl compounds with electron-rich alkenes are initiated by the π (alkene)–n (carbonyl addend) orbital interaction.[16] An electron (charge) transfer interaction from the filled π (alkene) orbital to the half-filled n (carbonyl compound) orbital is therefore inherently involved. As a result, the presence of an alkene π orbital with an energy higher than or close to the carbonyl n orbital can be taken as a prerequisite for efficient Paterno–Büchi reactions between triplet n–π* carbonyl compounds with alkenes. In line with this analysis, we have found that **1** could not take part in photoinduced cycloadditions with electron-deficient alkenes such as acrylonitrile and methyl acrylate which have a π orbital with a much lower energy (HOMO energy −10.9 eV[17] for acrylonitrile) than the n orbital of **1** (n orbital energy –9.253 eV). In contrast, alkenes **2**–**6** are all electron rich and have a π orbital of higher energy than the n orbital of **1**. As a matter of fact, the π orbital energy of styrene, which is the least electron rich of these alkenes, is ≈−9 eV.[18] However, although an unambiguous electron donor–acceptor relationship between the alkenes and the carbonyl moieties is required, the degree of electron (charge) transfer interaction will vary for different alkenes, depending on their oxidation potentials, and a full electron transfer characterized by the formation of polar exciplex or contact ion-radical pairs (CIPs) in non-polar solvents and of solvent-separated ion-radical pairs and free ions in polar solvents are not always energetically favorable. In this regard, the empirical Weller equations[19] can be conveniently used to estimate the SET energetics concerning the feasibility of the formation of polar exciplex (CIP) and ion-radical pairs. We have therefore calculated the free enthalpy for SET in these reactions by the Weller equations[19] (Table 2). Styrene **2** and α-methylstyrene **4** have large positive ΔG_{ET}-values in benzene. For these alkenes, ion-radical pair formation is thermodynamically unfeasible, and 1,4-diradicals are formed as the intermediate leading to the oxetane products. In these cases, the regioselectivity is rationalized by considering the FMO interactions of **1*** and the alkenes. For this purpose, an *ab initio*[24] calculation of the FMO energies and atomic coefficients of **1** has been carried out with the 6-31G basis set and the results are shown in Fig. 5. The FMO interactions between **1*** and styrene are shown in Fig. 6. It was seen that maximum positive FMO overlap in both HO–HO and LU–LU interactions requires a regioselectivity which is actually found in the products (**8** and **9**). α-Methylstyrene **4** and 1,1-diphenylethylene **3** have similar FMO characteristics as styrene,[17] and the FMO

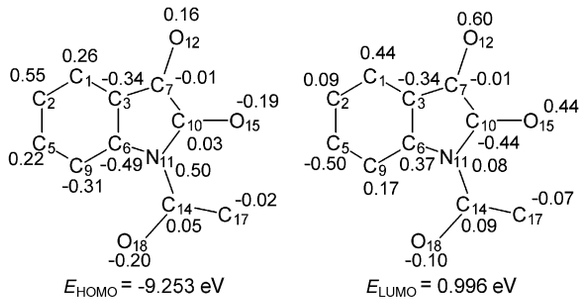


Fig. 5 FMOs of **1** calculated by 6-31G.

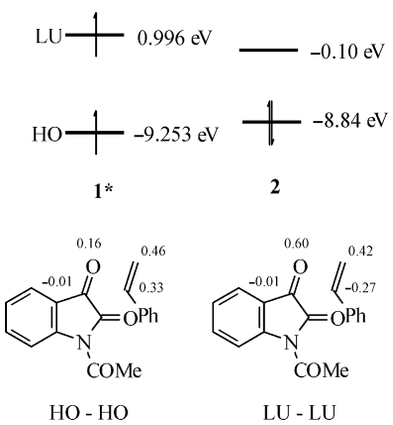
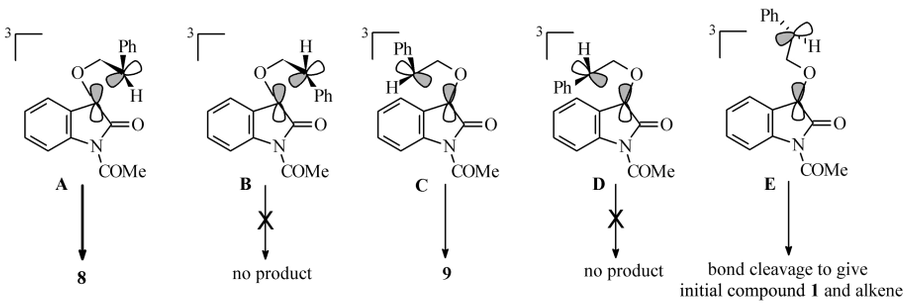


Fig. 6 FMO interactions between **1*** and **2**.

interactions are similar to those shown in Fig. 6, resulting in a regioselectivity in agreement with that seen in products **10**–**12**. It is also noted that the regioselectivity in products **9**–**12** was in accord with the most stable 1,4-diradical intermediates.

For the more electron-rich alkenes **3**, **5**, **6** and **7**, the negative ΔG_{ET}-values indicated the intervention of SET processes and the formation of contact ion-radical pairs as the primary event in the reactions carried out in benzene. In these cases, subsequent ion-radical pair recombination could take place either by radical pair coupling and C–C bond formation to give a zwitterion intermediate or by carbocation–oxyanion coupling and C–O bond formation to give a 1,4-diradical intermediate, depending on the charge and spin density distribution in the ion-radicals. The regioselectivity should therefore reflect a match of the charge and spin density distributions of the cation-radical of the alkenes and the anion-radical of **1**. This is seen to be the case in the reaction of **1** with **6**. We have carried out an AM1 calculation of the charge and spin density distributions in the cation-radical of **6**. The results are shown in Fig. 7. Since positive charge and spin density are both largely concentrated at C-2, and C-3 shares less charge and little spin density, C-2 should be the site of coupling with the oxyanion in $\mathbf{1}^{\bullet -}$ to give a 1,4-diradical intermediate as shown in structure **22**, the collapse of which gave the cycloadducts with a regioselectivity seen in products **16** and **17**. Since, in a benzyl-type radical, spin density delocalization to the phenyl ring is not as serious as positive charge delocalization to the phenyl ring in the corresponding benzyl cation, spin density is expected to be less delocalized than positive charge to the phenyl ring in the stilbene cation-radical, and this is substantiated by our AM1 calculation which showed that spin density was more heavily located at the two methylene carbon atoms than was charge density (Fig. 8). As a result, coupling of radical centers of $\mathbf{1}^{\bullet -}$ and $\mathbf{5}^{\bullet +}$ to give a 1,4-zwitterion intermediate **23** and coupling of charge centers to give a 1,4-diradical **24** are both possible.

It was also noted that, for these electron-rich alkenes (**3**, **5**, **6**), a drastic solvent polarity effect on the reactions occurred and the cycloadditions could not take place in the polar solvent acetonitrile where the ΔG_{ET}-values are negative. In these cases,



Scheme 1

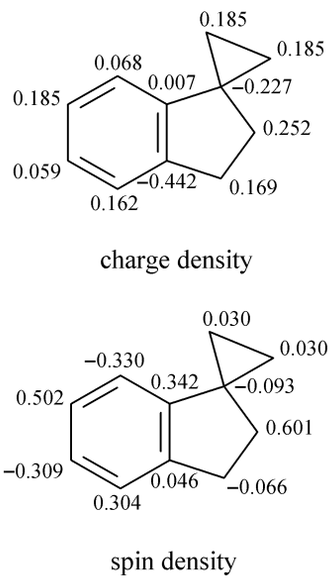


Fig. 7 Charge and spin density distribution in $\mathbf{6}^{\bullet+}$ by AM1 calculation.

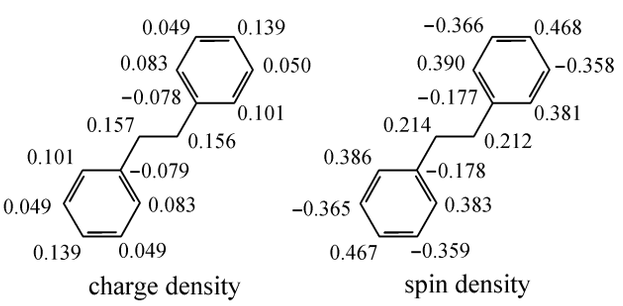


Fig. 8 Charge and spin density distribution in $\mathbf{5}^{\bullet+}$ by AM1 calculation.

further dissociation of the triplet ion-radical pairs prevails, and the intermolecular coupling leading to the cycloadducts is suppressed.[25]

2. Diastereoselectivity in the cycloadditions

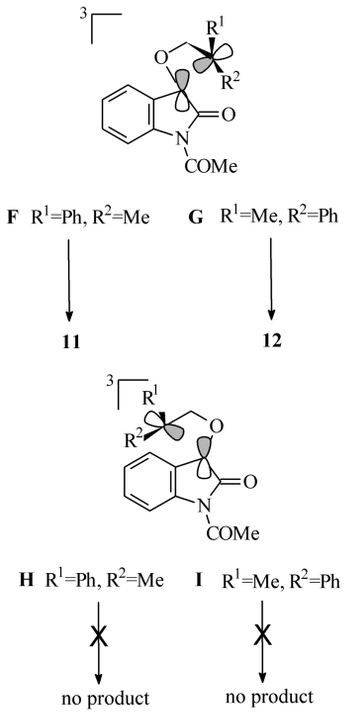
In Paterno–Büchi reactions, depending on the substitution pattern of the alkene, [2 + 2] cycloaddition of the C=O bond in a prochiral ketone with the C=C bond of the alkene resulted in the creation of two or three chiral centers and the formation of diastereoisomeric oxetane products. However, rationalization and prediction of the cycloaddition diastereoselectivity in view of the reaction mechanism have not received such extensive investigation[5,26] as has the regioselectivity. Griesbeck and coworkers have recently applied the long known Salem–Rowland rules[27] for intersystem crossing (ISC) of diradicals by the spin-orbit coupling mechanism to the 1,4-diradical intermediate in the Paterno–Büchi reaction to rationalize the addition diastereoselectivity, mainly in the reactions of different carbonyl compounds with cycloalkenes. In accordance with the first Salem–Rowland rule for ISC,[27] it was postulated that, among the possible conformations of the 1,4-diradical intermediate, only those in which the two spin-carrying p-orbitals are orthogonal to each other are responsible for efficient ISC, and bond rotation in these critical conformations leading to spin inversion therefore dictates the conformation of the singlet 1,4-diradical formed in the ISC. Since rapid bond formation immediately ensues once the singlet diradical is formed, the diastereoselectivity seen in the products is decided by conformations of the triplet 1,4-diradicals most suitable for ISC.

In the reactions of 1-acetylisatin with **2**–**7**, the oxidation potential of the alkene and the steric environment in the 1,4-diradical intermediate are modified by the change of substituent at the alkene C=C double bond, and this facilitates the search for the factors that affect the stereoselectivity.

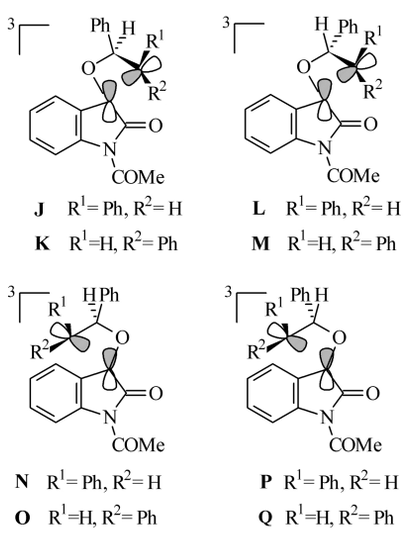
In the photocycloaddition of **1** to styrene **2**, the thermodynamically less favorable *syn* product was obtained in slight preference to the *anti* product. There are four conformers which have the two spin-bearing p-orbitals orthogonal to each other and are therefore suitable for rapid ISC and C–C bond formation. There are also four other conformers (such as **E**) which are suitable for efficient ISC but are not suitable for C–C bond formation because of the long distance between the two radical centers. These conformers would undergo rapid C–O bond cleavage to regenerate **1** and the alkene. These are shown in Scheme 1. In conformers **A** and **B**, the benzyl carbon atom approaches the original carbonyl carbon atom in **1** in the ISC and bond-forming processes from the outer side of the isatin framework. It is obvious that conformer **A** is sterically more favorable since there is no steric hindrance between the phenyl and the isatin framework as there is in **B**. ISC followed by bond formation in **A** gave the *syn* product **8**. On the other hand, in conformers **C** and **D**, the former is less sterically hindered than is **D**. ISC from **C** afforded the *anti* product **9**. The result that the *syn* product is preferentially formed over the *anti* product **9** may reflect the fact that the steric congestion between the hydrogen atom and the isatin phenyl ring in **C** would make it be less populated than conformer **A**.

In the reactions of **1** with α-methylstyrene **4** in benzene, conformers like **H** and **I** are unlikely to contribute to product formation considering the severe steric hindrance between the phenyl or methyl group and the isatin benzene ring. Conformers **F** and **G** both experience an increased steric strain over that in **A** (Scheme 1) by the *gauche* interaction between methyl (in **F**) or phenyl (in **G**) and the isatin carbonyl group at C-2, and the *syn*/*anti* quotient (0.61) can be viewed as a rough measure of the relative populations of these two conformers in relation to their thermodynamic stability (see Scheme 2).

Photocycloadditions of **1** with (*E*)-stilbene **5** display a different pattern of diastereoselectivity where the main product is the thermodynamically most stable isomer **15** with the two phenyls *trans* to each other. The other two stereoisomers **13** and **14** are formed as minor products. These results could not be rationalized by consideration of the 1,4-diradical conformers most suitable for ISC. Among the eight 1,4-diradical conformers which have the two p-orbitals orthogonal and close to each



Scheme 2



Scheme 3

other and are therefore suitable for ISC and C–C bond formation (conformers **J**–**Q**, Scheme 3), **J** and **L** are sterically least hindered and should be most heavily populated. However, ISC and subsequent bond formation from conformer **J** would lead to the formation of stereoisomer **13**, and ISC from **L** should give **14**, both of which are the minor products. The formation of the main product **15** would need a 1,4-diradical precursor **K** (Scheme 3) which is unlikely to be heavily populated because of the severe steric hindrance between the phenyl and the isatin framework.

The origin of this different diastereoselectivity for (*E*)-stilbene **5** from that found in the less electron-rich alkenes such as styrene **2** and α-methylstyrene **4** may be attributed to different reaction mechanisms. In the case of (*E*)-stilbene, ΔG_{ET} with ^{3}**1*** in benzene and in MeCN is estimated to be −1.8 and −12.1 kcal mol^{-1} respectively, indicating that an SET process is feasible in both solvents. This is also supported by the observed solvent polarity effect on the reactions. In the polar solvent acetonitrile, SET leads to the formation of triplet solvent-separated ion-radical pairs which tend to diffuse apart into free ions, and cycloadditions are therefore suppressed. SET interaction in benzene gives rise to exciplexes with high charge-transfer character which can be viewed as contact ion-radical pairs, and the two reactants are aligned in the CIP by coulombic interaction. Collapse of the ion-radical pairs may afford a zwitterion intermediate **23** by radical-pair coupling and C–C bond formation, and/or a 1,4-diradical intermediate **24** by ion-pair collapse and C–O bond formation. These intermediates then close to give the cycloaddition product. Since a diradical intermediate could be averted (at least in part), the diastereoselectivity is not entirely controlled by the same factors mentioned above for styrene **2** and α-methylstyrene **4** where SET processes and ion-radical-pair intermediates are not involved. If the zwitterion intermediate has a lifetime long enough for bond rotation to take place, the product with the two phenyls *trans* to each other as in **15** will predominate since it is the thermodynamically most stable product.

In summary, photoinduced cycloadditions of 1-acetylisatin **1** with alkenes **2**–**7** afforded spiroxetane products with high yields in most cases. The regioselectivity in the cycloadditions can be rationalized by considering the FMO interactions between the two addends and the most stable 1,4-diradical intermediates for reactions without SET involvement, and by considering charge and spin density distributions in the ion-radical pairs when SET *is* involved in the reactions. The diastereoselectivity also depends on the reaction mechanism. In reactions without ion-radical-pair formation (alkenes **2** and **4**), the Salem–Rowland rule for ISC can be applied to rationalize the diastereoselectivity by considering the 1,4-diradical intermediate most suitable for ISC. In reactions where SET takes place (*e.g.*, alkenes **3** and **5**), the diastereoselectivity is dictated by ion-radical pair-collapse pathways which lead to different intermediates *en route* to the cycloadducts.

Experimental

Mps were measured on a Yanaco microscopic melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker spectrometer at 300 MHz or on a Bruker AC-500 spectrometer at 500 MHz with $SiMe_4$ as internal standard and $CDCl_3$ as solvent unless otherwise stated. *J*-Values are given in Hz. IR spectra were taken with a Shimadzu IR 440 spectrometer for samples in KBr pellets. Mass spectra were recorded with a VG ZAB-MS spectrometer. Elemental analyses were obtained using a Perken-Elmer 240 C analyser. Acetonitrile (CP grade) was first refluxed with phosphorus pentaoxide and distilled, then refluxed with anhydrous potassium carbonate and re-distilled. Benzene (AR grade) was dried with sodium and distilled before use. Other reagents were CP or AR grade and were used as received without further purification. Petroleum spirit was the fraction with distillation range 60–90 °C.

Cyclic voltammetric measurements

Oxidation potential of alkenes **6** and **7** and the reduction potential of *N*-acetylisatin **1** were measured by cyclic voltammetry in dry acetonitrile with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. Platinum electrodes were used as working and auxiliary electrode; the reference electrode was an SCE. The scan speed was 100 mV s^{-1} for oxidation potential measurement and 50 mV s^{-1} for $E^{red}_{1/2}$ measurement. The solutions were ≈0.1–1 mM in the substrate and were purged with dry nitrogen for 10 min before measurements to remove dissolved oxygen.

General procedures for the preparative photolyses of 1-acetylisatin 1 with alkenes

The light source was a medium-pressure mercury lamp (500 W) in a cooling water jacket which was further surrounded by a layer of filter solution (10% aq. sodium nitrite; 1 cm thickness;

$\lambda > 400$ nm). The solution of 1-acetylisatin **1** and an excess of alkene in benzene (60 ml) was placed in three glass tubes (20 ml each) and purged with dry argon for 30 min. The solutions were then irradiated with $\lambda > 400$ nm at room temperature under continuous argon purging. At the end of the reaction (TLC monitoring) the solvent was removed *in vacuo* and the residue was separated by flash chromatography on a silica gel column with petroleum spirit–ethyl acetate as eluent for gradient elution to afford the cycloaducts as a mixture of stereoisomers, which was subjected to ^{1}H NMR (300 or 500 MHz) measurement for determination of the product ratio. The reaction time, the total yield and the product ratio are listed in Table 1. Pure samples of the isomers were obtained by using the procedures described as follows.

Photolysis of 1 with styrene 2. *In benzene.* A solution of **1** (388 mg, 2.0 mmol) and **2** (2080 mg, 20 mmol) in benzene (40 ml) was photolysed for 7 h to lead to a 100% conversion of **1**. Work-up as before afforded a mixture of **8** and **9** (96%) in the ratio 1.42 : 1 as estimated from the 300 MHz ^{1}H NMR spectrum of the mixture. The mixture of **8** and **9** was subjected to stepwise crystallization from petroleum spirit–ethyl acetate to give pure samples of the two isomers.

In acetonitrile. Under the same conditions, reaction of **1** and **2** in acetonitrile for 24 h gave the mixture of **8** and **9** in the ratio 2.57 : 1.

(3R,3′R)-1-Acetyl-1,2-dihydro-2-oxo-3′-phenylspiro[3H-indole-3,2′-oxetane] **8**. Colorless prisms from petroleum spirit–ethyl acetate, mp 108–109 °C; λ_{max} 245 nm (ε 1.33 × 10^5 l mol^{-1} cm^{-1}); ν_{max}/cm^{-1} 3040, 2980, 2900, 1772, 1700, 1608, 1460, 1375, 1340, 1282, 1265, 1162, 1105, 1028, 985, 950, 756, 717, 700, 595; δ_H (500 MHz) 2.76 (3H, s), 4.71 (1H, t, *J* 7.7), 5.25 (1H, t, *J* 6.5), 5.38 (1H, dd, *J* 7.7, 6.5), 6.92 (1H, t, *J* 7.6), 7.03 (3H, m), 7.19–7.28 (4H, m), 8.15 (1H, d, *J* 8.1); *m*/*z* (%) 293 (M$^+$, 0.15), 263 (22), 221 (83), 165 (59), 104 (100) (Found: C, 73.84; H, 5.25; N, 4.69. $C_{18}H_{15}NO_3$ requires C, 73.72; H, 5.12; N, 4.78%).

(3R,3′S)-1-Acetyl-1,2-dihydro-2-oxo-3′-phenylspiro[3H-indole-3,2′-oxetane] **9**. Colorless prisms from petroleum spirit–ethyl acetate, mp 105–106 °C; ν_{max}/cm^{-1} 3020, 2980, 2900, 1772, 1702, 1608, 1460, 1375, 1340, 1300, 1278, 1264, 1198, 1164, 1110, 1035, 1012, 992, 955, 767, 755, 700, 600; δ_H (500 MHz) 2.29 (3H, s), 4.79 (1H, t, *J* 9.1), 4.94 (1H, dd, *J* 9.1, 5.6), 5.60 (1H, dd, *J* 9.1, 5.6), 7.05 (2H, d, *J* 7.3), 7.23–7.30 (3H, m), 7.36 (1H, t, *J* 7.5), 7.44 (1H, d, *J* 8.0), 7.81 (1H, d, *J* 7.5), 8.18 (1H, d, *J* 8.0); *m*/*z* (%) 293 (M$^+$, 0.14), 263 (29), 221 (100), 193 (53), 165 (53), 104 (77) (Found: C, 73.76; H, 5.19; N, 4.72%).

Photolysis of 1 with 1,1-diphenylethylene 3 in benzene. A solution of **1** (388 mg, 2.0 mmol) and 1,1-diphenylethylene **3** (3600 mg, 20 mmol) in benzene (40 ml) was photolysed for 16 h to lead to a 100% conversion of **1**. Work-up as before afforded **10** (98%).

1-Acetyl-1,2-dihydro-2-oxo-3′,3′-diphenylspiro[3H-indole-3,2′-oxetane] **10**. Colorless crystals from petroleum spirit–ethyl acetate, mp 139–141 °C; ν_{max}/cm^{-1} 3050, 2970, 2900, 1762, 1698, 1604, 1462, 1376, 1340, 1303, 1280, 1170, 1104, 1032, 1015, 998, 760, 718, 598; δ_H (60 MHz) 2.49 (3H, s), 5.53 (1H, d, *J* 6.0), 6.08 (1H, d, *J* 6.0), 6.47–7.67 (13H, m), 8.29 (1H, d, *J* 8.0); *m*/*z* (%) 339 (0.16), 297 (0.27), 206 (0.15), 189 (24), 180 (99), 146 (100) (Found: C, 78.07; H, 5.31; N, 3.71. $C_{24}H_{19}NO_3$ requires C, 78.05; H, 5.15; N, 3.79%).

Photolysis of 1 with α-methylstyrene 4. *In benzene.* A solution of **1** (388 mg, 2.0 mmol) and α-methylstyrene **4** (2360 mg, 20 mmol) in benzene (40 ml) was photolysed for 14 h to lead to a 100% conversion of **1**. Work-up as before afforded a mixture of **11** and **12** (96%) in the ratio of 1 : 1.64 as estimated from the 300 MHz ^{1}H NMR spectrum of the mixture. The mixture of **11** and **12** was subjected to stepwise crystallization from petroleum spirit–ethyl acetate to give the pure sample of **11**.

In acetonitrile. Under the same conditions, reaction of **1** and **4** in acetonitrile for 24 h gave a mixture of **11** and **12** in the ratio 2.19 : 1.

(3R,3′R)-1-Acetyl-1,2-dihydro-3′-methyl-2-oxo-3′-phenylspiro[3H-indole-3,2′-oxetane] **11**. Colorless plates from petroleum spirit–ethyl acetate, mp 149–150 °C; ν_{max}/cm^{-1} 3050, 2960, 2900, 1762, 1700, 1604, 1460, 1380, 1338, 1300, 1280, 1160, 1102, 1030, 1010, 982, 762, 703, 600; δ_H (500 MHz) 1.77 (3H, s), 2.75 (3H, s), 4.97 (1H, d, *J* 5.9), 5.41 (1H, d, *J* 5.9), 6.60 (1H, d, *J* 7.4), 6.78–6.82 (3H, m), 7.14–7.22 (4H, m), 8.15 (1H, d, *J* 8.2); *m*/*z* (%) 307 (M$^+$, 0.37), 277 (7.0), 235 (20), 189 (6.0), 118 (100) (Found: C, 74.41; H, 5.56; N, 4.65. $C_{19}H_{17}NO_3$ requires C, 74.27; H, 5.54; N, 4.56%).

(3R,3′S)-1-Acetyl-1,2-dihydro-3′-methyl-2-oxo-3′-phenylspiro[3H-indole-3,2′-oxetane] **12**. Not fully separated from isomer **11**; δ_H (300 MHz) 1.75 (3H, s), 2.12 (3H, s), 4.48 (1H, d, *J* 5.0), 5.83 (1H, d, *J* 5.0), 6.79–7.47 (7H, m), 7.76 (1H, d, *J* 8.2), 8.27 (1H, d, *J* 8.1).

Photolysis of 1 with stilbenes 5. *In benzene.* A solution of **1** (388 mg, 2.0 mmol) and (*E*)-stilbene (540 mg, 3.0 mmol) in benzene (40 ml) was photolysed for 36 h to lead to a 58% conversion of **1**. Work-up as before afforded a mixture of **13**, **14** and **15** (56%) in the proportions 2.9 : 1 : 8.2 as estimated from the 300 MHz ^{1}H NMR spectrum of the mixture. The mixture of **13**, **14** and **15** was subjected to stepwise crystallization from petroleum spirit–ethyl acetate to give a pure sample of **13**.

In acetonitrile. Under the same conditions, reaction of **1** and **5** in acetonitrile for 24 h to lead to <1.5% conversion of **1** and gave a mixture of **13**, **14** and **15** in the proportions 1 : 1.4 : 5.

Photolysis of 1 with (*Z*)-stilbene. Under the same conditions, reaction of **1** and (*Z*)-stilbene in benzene for 24 h gave a mixture of **13**, **14** and **15** in the proportions 1.2 : 1 : 8.

(3R,3′S,4′S)-1-Acetyl-1,2-dihydro-2-oxo-3′,4′-diphenylspiro[3H-indole-3,2′-oxetane] **13**. Colorless crystals from petroleum spirit–ethyl acetate, mp 186–187 °C; ν_{max}/cm^{-1} 3020, 2960, 2900, 1760, 1710, 1610, 1495, 1460, 1368, 1332, 1310, 1280, 1168, 1018, 978, 756, 712, 700; δ_H (300 MHz) 2.80 (3H, s), 5.05 (1H, d, *J* 8.8), 6.70 (2H, d, *J* 7.0), 6.80 (1H, d, *J* 8.8), 6.97–7.04 (4H, m), 7.25–7.41 (7H, m), 8.16 (1H, d, *J* 8.2); *m*/*z* (%) 369 (M$^+$, 0.42), 327 (0.97), 263 (36), 221 (79), 181 (100), 166 (58) (Found: C, 78.13; H, 5.22; N, 3.68. $C_{24}H_{19}NO_3$ requires C, 78.05; H, 5.15; N, 3.79%).

(3R,3′S,4′R)-1-Acetyl-1,2-dihydro-2-oxo-3′,4′-diphenylspiro-[3H-indole-3,2′-oxetane] **14**. Not fully separated from isomers **13** and **15**; δ_H (300 MHz) 2.80 (3H, s), 4.94 (1H, d, *J* 8.2), 6.42 (1H, d, *J* 8.2), 6.85–7.52 (13H, m), 7.93 (1H, d, *J* 7.6).

(3R,3′R,4′S)-1-Acetyl-1,2-dihydro-2-oxo-3′,4′-diphenylspiro[3H-indole-3,2′-oxetane] **15**. Not fully separated from isomers **13** and **14**; δ_H (500 MHz) 2.37 (3H, s), 4.61 (1H, d, *J* 8.6), 6.69 (1H, d, *J* 8.6), 7.123 (2H, d, *J* 7.5), 6.97–7.50 (8H, m, ArH), 7.664 (2H, d, *J* 7.5), 7.85 (1H, d, *J* 7.5), 8.22 (1H, d, *J* 8.2).

Photolysis of 1 with spirocyclopropane-1,1′-[1*H*]indene 6 in benzene. A solution of **1** (388 mg, 2.0 mmol) and spirocyclopropane-1,1′-indene **6** (852 mg, 6.0 mmol) in benzene (40 ml) was photolysed for 8 h to lead to a 100% conversion of **1**. Work up as before afforded a mixture of **16** and **17** (90%) in the ratio 6 : 1 as estimated from the 300 MHz ^{1}H NMR spectrum. The mixture was subjected to stepwise crystallization from petroleum spirit–ethyl acetate to give a pure sample of **16**.

(2′aS,3″R,7′aS)-1″-Acetyl-1″,2′a,2″,7′a-tetrahydro-2″-oxodispiro{cyclopropane-1,7′-2′H-indeno[2,3-b]oxetane-2′,3″-3″H-indole} **16**. Colorless needles from petroleum spirit–ethyl acetate, mp 172–173 °C; λ_{max} 245 nm (ε 1.33 × 10^5 l mol^{-1} cm^{-1});

ν_{max}/cm^{-1} 2950, 1760, 1700, 1600, 1460, 1365, 1340, 1330, 1300, 1282, 1262, 1164, 1100, 957, 760; δ_H (500 MHz) 1.00–1.04 (1H, m), 1.16–1.20 (1H, m), 1.27–1.30 (1H, m), 1.49–1.53 (1H, m), 2.76 (3H, s), 4.54 (1H, d, *J* 5.1), 5.46 (1H, d, *J* 5.1), 6.18 (1H, d, *J* 7.6), 6.69 (1H, d, *J* 7.6), 6.87 (1H, t, *J* 7.6), 6.90 (1H, d, *J* 7.6), 7.10 (1H, t, *J* 7.6), 7.30 (1H, t, *J* 7.6), 7.34 (1H, t, *J* 7.6), 8.18 (1H, d, *J* 7.6); *m*/*z* (%) 331 (M^+, 1.9), 289 (4.5), 217 (4.3), 189 (2.4), 142 (100) (Found: C, 76.15; H, 5.27; N, 4.17. $C_{21}H_{17}NO_3$ requires C, 76.13; H, 5.14; N, 4.23%).

(2′aS,3″R,7′aR)-1″-Acetyl-1″,2′a,2″,7′a-tetrahydro-2″-oxodispiro{cyclopropane-1,7′-2′H-indeno[2,3-b]oxetane-2′,3″-3″H-indole} **17**. Not fully separated from isomer **16**; δ_H (500 MHz) 1.04–1.08 (1H, m), 1.11–1.16 (1H, m), 1.31–1.36 (1H, m), 1.61–1.66 (1H, m), 2.42 (3H, s), 4.53 (1H, d, *J* 5.1), 5.26 (1H, d, *J* 5.1), 6.85–6.87 (1H, m), 6.98 (1H, d, *J* 7.6), 7.17 (1H, t, *J* 7.6), 7.28–7.34 (2H, m), 7.43 (1H, t, *J* 7.6), 7.82 (1H, d, *J* 7.6), 8.25 (1H, d, *J* 7.6).

Photolysis of 1 with 7 in benzene. Under the above conditions, a solution of **1** (567 mg, 3 mmol) and 9-(diphenylmethylene)-1,4-dihydro-1,4-methanonaphthalene **7** (1100 mg, 3.6 mmol) in benzene (60 ml) was photolysed for 18 h to lead to the total conversion of **1** and afforded **18** (145 mg, 10%), **19** (510 mg, 34%), and a mixture of **20** and **21** (380 mg, 26%) in the ratio 2 : 1 as estimated from the 500 MHz ^{1}H NMR spectrum of the mixture.

Photolysis of 1 with 7 in acetonitrile. Under the above conditions, a solution of **1** (567 mg, 3 mmol) and compound **7** (1100 mg, 3.6 mmol) in acetonitrile (60 ml) was photolysed for 60 h to lead to the total conversion of **1** and afforded benzophenone (150 mg), **18** (15 mg, 1%), **19** (90 mg, 6%), and a mixture of **20** and **21** (440 mg, 30%) in the ratio of 2 : 1 as estimated from the 500 MHz ^{1}H NMR spectrum of the mixture.

(2′aR,3S,3′R,8′S,8′aS)-1-Acetyl-9′-diphenylmethylene-1,2,2′a,3′,8′,8′a-hexahydro-2-oxospiro{3H-indole-3,2′-(2′H-3′,8′-methanonaphtho[2,3-b]oxete)} **18**. Recrystallization from petroleum spirit–chloroform gave colorless blocks, mp 232 °C; δ_H (500 MHz) 2.66 (3H, s), 2.97 (1H, d, *J* 4.6), 4.19 (1H, s), 4.42 (1H, s), 5.41 (1H, d, *J* 4.6), 6.74 (1H, t, *J* 7.6), 7.13–7.45 (15H, m), 7.78 (1H, d, *J* 7.6), 8.15 (1H, d, *J* 8.2); ν_{max}/cm^{-1} 3050, 1780, 1710, 1600, 1460, 1370, 1340, 1280, 1172, 1100, 1015, 950, 760, 705; *m*/*z* 495 (M^+, 9), 466 (33), 346 (24), 280 (100) (Found: C, 82.35; H, 5.28; N, 2.79%).

(2′aR,3S,3′S,8′R,8′aS)-1-Acetyl-9′-diphenylmethylene-1,2,2′a,3′,8′,8′a-hexahydro-2-oxospiro{3H-indol-3,2′-(2′H-3′,8′-methanonaphtho[2,3-b]oxete)} **19**. Recrystallization from petroleum spirit–chloroform gave colorless prisms; mp 253 °C; δ_H (500 MHz) 2.22 (3H, s), 2.88 (1H, d, *J* 4.6), 4.20 (1H, s), 4.45 (1H, s), 5.18 (1H, d, *J* 4.6), 7.16–7.59 (17H, m), 8.13 (1H, d, *J* 8.4); ν_{max}/cm^{-1} 3050, 1780, 1705, 1600, 1485, 1370, 1340, 1272, 1163, 1100, 1020, 760, 705; *m*/*z* (%) 495 (M^+, 10), 423 (24), 346 (35), 280 (73), 167 (75), 57 (100) (Found: C, 82.42; H, 5.46; N, 2.58. $C_{34}H_{25}NO_3$ requires C, 82.42; H, 5.20; N, 2.83%).

1-Acetyl-1,1″,2,4″-tetrahydro-2-oxo-3′,3′-diphenyldispiro[3H-indole-3,2′-oxetane-4′,9″-(1″,4″-methanonaphthalene)] **20**. Not fully separated from isomer **21**. δ_H (500 MHz) 2.44 (3H, s), 4.33 (1H, s), 4.83 (1H, s), 6.35 (1H, d, *J* 7.0), 6.89–7.40 (18H, m), 8.22 (1H, d, *J* 8.1).

21. Not fully separated from isomer **20**. δ_H (500 MHz) 2.60 (3H, s), 4.66 (1H, s), 4.93 (1H, s), 6.89–7.40 (19H, m), 8.26 (1H, d, *J* 8.2).

Crystal structure of compound 8 ‡

$C_{18}H_{15}NO_3$, *M* = 293.31. Monoclinic, space group *P*21/*c*, *Z* = 4, *a* = 9.4575(2), *b* = 17.2629(3), *c* = 9.2678(1) Å, *α* = 90°, *β* = 98.894(1)°, *γ* = 90°, *V* = 1494.90(4) Å^3, *Dc* = 1.303 g cm^{-3}. Data were collected on a Siemens SMART CCD area detector diffractometer equipped with graphite-monochromatized Mo-Kα in the range of *θ* = 2.18–28.28°. A total of 3631 independent reflections [*R*(int) = 0.0690] were used in the refinement which converged with *R* = 0.0524 and *wR* = 0.1372 (GOF = 0.895).

Crystal structure of compound 11 ‡

$C_{19}H_{17}NO_3$, *M* = 307.34. Monoclinic, space group *P*21/*c*, *Z* = 4, *a* = 8.1254(4), *b* = 25.2801(14), *c* = 8.1544(5) Å, *α* = 90°, *β* = 110.812(1)°, *γ* = 90°, *V* = 1565.71(15) Å^3, *Dc* = 1.304 g cm^{-3}. Data were collected on a Siemens SMART CCD area detector diffractometer equipped with graphite-monochromatized Mo-Kα in the range of *θ* = 2.18–28.28°. A total of 3789 independent reflections [*R*(int) = 0.0799] were used in the refinement which converged with *R* = 0.0736 and *wR* = 0.1646 (GOF = 0.915).

Crystal structure of compound 13 ‡

$C_{24}H_{19}NO_3$, *M* = 369.40. Monoclinic, space group *P*21/*c*, *Z* = 4, *a* = 9.9020(4), *b* = 8.9865(3), *c* = 22.1097(6) Å, *α* = 90°, *β* = 97.750(2)°, *γ* = 90°, *V* = 1949.45(12) Å^3, *Dc* = 1.259 g cm^{-3}. Data were collected on a Siemens SMART CCD area detector diffractometer equipped with graphite-monochromatized Mo-Kα in the range of *θ* = 2.18–28.28°. A total of 4737 independent reflections [*R*(int) = 0.0942] were used in the refinement which converged with *R* = 0.0617 and *wR* = 0.1345 (GOF = 0.846).

‡ CCDC reference number 207/495. See http://www.rsc.org/suppdata/p1/b0/b005576j/ for crystallographic files in .cif format.

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