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THE GENERATION AND PHOTOCHEMISTRY OF INDENONE O-OXIDE AND FLUORENONE O-OXIDE IN LOW TEMPERATURE MATRICES

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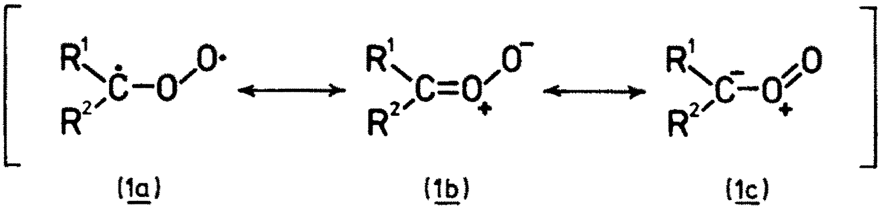
Abstract: The photolysis of diazoindene and diazofluorene at 12K in N_2 matrices containing O_2 has been studied, using i.r. spectroscopy. The carbonyl oxides, indenone O-oxide and fluorenone O-oxide, were formed by the reaction of O_2 with the corresponding carbenes, and under appropriate conditions could be detected as very photolabile species. Photolysis of indenone O-oxide gave indenone and isocoumarin; similar photolysis of fluorenone O-oxide gave fluorenone and dibenzopyran-6-one.

Carbonyl oxides (1) have long been supposed to occur as reactive intermediates in ozonolysis,[1] and in the oxidation of diazo compounds,[2,3] and have aroused interest because of their ability to transfer oxygen atoms to other substrates.[3,4] More recently, additional interest in these species has centred on their direct spectroscopic detection and characterization. Successes in this direction have included the isolation of cyclopentadienone O-oxide in low-temperature matrices and the observation of its u.v.-visible and i.r. absorption spectra.[5,6] U.v.-visible detection of matrix isolated tetrachlorocyclopentadienone O-oxide, indenone O-oxide, and fluorenone O-oxide has also been achieved.[6] Flash photolysis studies have led to the observation of transient u.v.-visible absorptions attributed to 10,10-dimethyl-10-sila-anthracen-9-[10H]-one O-oxide,[7] benzophenone O-oxide,[8] and fluorenone O-oxide.[9] The photochemistry of carbonyl oxides has been examined, and in the cases published so far, appears to involve either the ejection of an oxygen atom to yield the corresponding ketone, or rearrangement to yield one or more of a variety of molecules which retain both oxygen atoms.[5,7,10]



(1a) (1b) (1c)

Matrix isolation studies of the photolysis of diazoindene (2) and diazofluorene (5) have recently been made in our laboratories. The carbenes, indenylidene and fluorenylidene, have been characterized by u.v.-visible and i.r. spectroscopy, and their reactions with CO observed.[11] We have also reported a u.v.-visible spectroscopic study of the matrix reactions of indenylidene and fluorenylidine with O_2.[6] We now describe further investigations, making use of i.r. spectroscopy, of the photolysis of diazoindene and diazofluorene at 12K in N_2 matrices containing O_2. In these conditions, a reaction between O_2 and the corresponding carbenes takes place, and the i.r. spectra of the adducts, indenone O-oxide and fluorenone O-oxide, have been recorded. The subsequent photolysis of these carbonyl oxides has also been examined.

EXPERIMENTAL

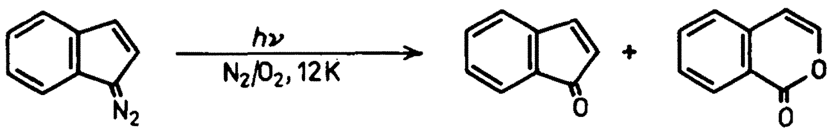
General Procedure.- The matrix isolation technique used in this research and its applications to structural and mechanistic problems in organic chemistry have been reviewed elsewhere.[12] The technique consists of trapping molecules of a guest species in a large excess of a solidified inert host-gas, such as Ar or N_2, at very low temperatures (typically 4-20K). These Ar or N_2 matrices have no host-gas absorptions throughout the normal u.v.-visible (200-700 nm) or i.r. (4000-400 cm^{-1}) regions of the spectrum, and are thus ideal for spectroscopic studies. Moreover, photolysis of matrix isolated molecules allows the observation, by ordinary spectroscopic means, of fragment molecules, such as radicals, carbenes, and nitrenes, or highly reactive species, such as cyclobutadiene and benzyne.[12] Thermal reactions between two matrix isolated molecules may often be induced by annealing (warming and re-cooling) the matrices at temperatures where softening occurs (typically 30-40K). A combination of these methods has been used in this work.

Equipment.- The low temperature cell has been described in detail previously.[13] It consisted of a CsBr window enclosed in a glass and metal vacuum shroud and cooled by an Air Products Displex CSA-202 closed cycle helium refrigerator. The base temperature was 12K, and higher temperatures could be achieved by means of a small resistance heater connected to an Air Products APD-B temperature controller. I.r. spectra were recorded on unmodified JASCO model IRA-2 and Perkin Elmer model 684 spectrometers, the latter interfaced with a Perkin Elmer model 3600 Data Station. Photolysis was carried out with a Philips HPK 125W medium pressure Hg arc or an Oriel 200 W high pressure Hg arc. In all circumstances, a water filter (13 cm pathlength) with quartz windows ($\lambda > 200$ nm) was used to remove i.r. radiation. Additional filtration, provided by pyrex ($\lambda > 300$ nm), soda glass ($\lambda > 330$ nm), or interference filters ($\lambda = 296 \pm 5$, 312 ± 5, or 365 ± 5 nm), was used as necessary.

Materials.- Research grade N_2 ($\not< 99.994\%$) and O_2 ($\not< 99.97\%$) were obtained from B.O.C. Ltd., and were used without further purification. Diazoindene (2),[14] diazofluorene (5),[15] indenone (3),[16] isocoumarin (4),[17] and dibenzopyran-6-one (7)[18] were all prepared by literature methods. Fluorenone (6) was obtained as a commercial sample.

Matrix deposition.- Mixtures of N_2 and O_2 were prepared, as required and in known ratios, by standard manometric techniques. Because of their low volatility, all the compounds studied in this investigation were incorporated into matrices by direct sublimation on to the cold window at 20K, with simultaneous deposition of a stream of host-gas, controlled by a fine needle-valve. For the least volatile materials, (4), (5), (6), and (7), the stream of host gas was allowed to pass directly over the crystals of guest compound, which were contained in a side-arm attached to the vacuum shroud of the cold cell. In these circumstances, matrix ratios (host:guest) could not be estimated. Matrices were cooled to 12K immediately after deposition.

Scheme 1.



(2) (3) (4)

RESULTS

Two diazo compounds, diazoindene (2) and diazofluorene (5), have been isolated and photolysed in O_2-doped N_2 matrices at 12K. The reactions were monitored by i.r. spectroscopy, and the results for each compound will be described separately.

Diazoindene (2).- Wide-band irradiation ($\lambda > 330$ nm) of (2) at 12K in N_2 containing 10% O_2 resulted, after 20 min, in almost complete disappearance of the i.r. bands of (2) [ν(CNN) 2086 cm^{-1}] and the appearance of a complex new i.r. spectrum. The main products of this reaction were indenone (3) and isocoumarin (4), identified by comparison of the product i.r. spectrum with those of authentic (3) and (4) isolated in N_2 matrices. Table 1 comprises a detailed comparison of the spectra. Small frequency differences (up to ±5 cm^{-1}) between O_2-doped and pure N_2 matrices were apparent for some of the bands. The larger differences within these limits were certainly greater than estimated variations of experimental reproducibility (±2 cm^{-1}), but were typical, in our experience, of the small matrix shifts induced by the presence of O_2. All of the strong and medium intensity bands and over a third of the weak bands of (3) and (4) were identifiable in the product spectrum, with surprisingly few overlaps, and with a reasonable match of relative intensities also. Only three weak bands in the product spectrum appeared not to belong to either (3) or (4). These occurred at 1387, 1352, and 1160 cm^{-1}, and could not be assigned to any obvious third product. They did not belong to indenylidene (8), whose matrix i.r. spectrum has recently been observed,[11] or to the carbonyl oxide (9) (see below). In addition to (3) and (4), CO_2 (2347 and 661 cm^{-1}) was also observed as a product in this photolysis. Its concentration, however, continued to increase on irradiation, even after all the diazoindene had disappeared. CO_2 was, therefore, a secondary photolysis product. In an effort to ascertain the origin of the CO_2, both indenone (3) and isocoumarin (4) were irradiated (λ>330 nm) separately in pure N_2 matrices, but neither compound gave any detectable CO_2 nor appeared to photolyse. It was found, however, that irradiation of (4) in O_2-doped N_2 matrices did result in CO_2 formation. With O_2 levels of 1%, the photolysis was slow but discernible, while higher concentrations of O_2 increased the rate of CO_2 formation significantly. It appeared, therefore, that some kind of secondary photo-oxidation reaction was responsible for the observed CO_2 in the photolysis of (2), rather than a unimolecular decomposition of (4).

TABLE 1.

I.r. bands (cm^{-1}), in the region 2000–400 cm^{-1}, of the photoproducts from (2) in O_2-doped N_2 matrices, and of authentic (3) and (4) in N_2 matrices.

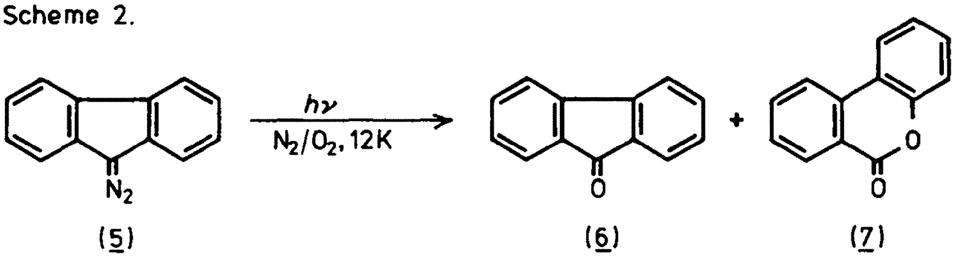
Photoproducts from (2)	(3)	(4)	Photoproducts from (2)	(3)	(4)
		1779			1193
1760s†		1759s	1184	1183	
1749s		1746s		1177	
1724s	1729s		1160		
		1736		1151	
1717s	1722s			1140	
		1712	1118		1117
1642		1641m	1106	1105	
1612m	1615m			1080	
		1605	1056		1055m
	1600		1047		1047m
1547	1549		1040	1039	
1491		1490m		1033	
	1479		1014	1015	1014
	1467		1003	1005	1001m
1457		1455		983	
	1447			974	
	1415			891	
1387				827	
1370	1371		795		794m
1352			781		780
1333	1328m		770m	770m	
		1322	758m	761m	
1315		1315m			750
	1311				719
1288	1285m		714	714	
1280	1277m	1279m	692		692m
1254m		1253s			495
1242	1246			462	
1231		1231			439
1208	1205	1207			407

†Qualitative band intensities: bands were weak unless denoted s (strong) or m (medium).

The photolysis of (2) ($\lambda > 330$ nm) in N_2 matrices containing only 0.1% O_2 produced a small concentration of indenylidene (8) (strongest bands at 1305, 1302, 751, and 741 cm^{-1})[11] as well as (3) and (4). When the matrix was annealed, a deterioration in its optical quality and i.r. band-broadening resulted, but a new i.r. band at 912 cm^{-1} was seen to have arisen. Other, minor changes in the spectrum were less definite. With N_2 matrices containing 1% O_2, no indenylidene could be detected after photolysis of (2).

Irradiation of (2) (N_2 matrix containing 10% O_2) with narrow-band 312 nm light (105 min) photolysed most of the diazo compound and gave a new product along with (3) and (4). This new species had i.r. bands at 1465, 1076, 938, 912 m, 852, 634, and 488 cm^{-1} (weak except as noted), and was probably the same species that was formed during the annealing experiment described above. Subsequent wide-band irradiation ($\lambda > 330$ nm) removed the new species within 30s, and an accompanying increase in the absorptions of (3) and (4) was noted. Irradiation with 312 nm light, therefore, produced a photolabile precursor of (3) and (4).

Scheme 2.



Diazofluorene (5).- Our results with diazofluorene were very similar to those we obtained with diazoindene. Wide-band irradiation ($\lambda > 330$ nm) of (5) at 12K in N_2 containing 10% O_2 resulted, after 10 min, in almost complete photolysis of (5) [ν(CNN) 2070 cm^{-1}] and the formation of fluorenone (6) and dibenzopyran-6-one (7). The products were identified by comparison of the product i.r. absorptions with those of authentic (6) and (7) isolated in pure N_2 matrices at 12K [Table 2]. All the strong and medium intensity i.r. bands of (6) and (7) and a good proportion of the weaker ones were recognized in the product spectrum, although some overlapping occurred. Small frequency shifts (up to ±6 cm^{-1}) in the O_2-doped matrix spectrum were apparent for some of the bands, and were attributed to perturbations by O_2 (see above). Only three weak product bands, at 1370, 1219, and 814 cm^{-1}, could not be assigned to (6) or (7). These bands did not belong to fluorenylidene (16), whose matrix i.r. spectrum has recently been observed,[11] or to the carbonyl oxide (17) (see below). A small amount of CO_2 was also produced in this reaction, but irradiation of (7) ($\lambda > 330$ nm) in N_2 or O_2-doped N_2 matrices did not result in the formation of CO_2, so its origin in the photo-oxidation of (5) is not yet clear.

Photolysis of (5) ($\lambda > 330$ nm) in N_2 matrices containing only 0.1% O_2 probably produced a small concentration of fluorenylidene (16) (strongest bands at 1035 and 755 cm^{-1}),[11] but overlap with other bands in the spectrum made this difficult to decide with certainty. When the matrix was annealed, growth of an i.r. band at 898 cm^{-1} was barely perceptible amongst general band-broadening.

Irradiation of (5) (N_2 matrix containing 10% O_2) with narrow-band 312 nm light (29 min) resulted in almost complete photolysis of (5). Three photoproducts were formed: fluorenone (6), dibenzopyran-6-one (7), and a third species with i.r. absorptions at 975, 898 m, 881, 783, 770, and 732 cm^{-1}. The 898 cm^{-1} band, seen to grow in the annealing experiment (see above), probably belonged to the same species. Subsequent wide-band irradiation ($\lambda > 200$ nm) for 15s removed the new species and increased the intensity of the i.r. bands due to (6) and (7). Irradiation with 312 nm light, therefore, produced on photolabile precursor of (6) and (7).

TABLE 2.

I.r. bands (cm^{-1}), in the region 2000-400 cm^{-1}, of the photoproducts from (5) in O_2-doped N_2 matrices, and of authentic (6) and (7) in N_2 matrices.

Photoproducts from (5)	(6)	(7)	Photoproducts from (5)	(6)	(7)
		1782	1195	1194m	
1764s†		1765s		1183	
1753s		1756s	1154	1152	
1738		1734			1130
1729s	1730s				1107
1700	1703			1101	
1616m	1616s	1613m	1098 }		1096m
1599s	1605m	1599m	1097 }		
		1509		1092	
1491		1490m	1078		1080s
1456m	1455m	1461m	1039m		1035m
1437		1438m	918m	919s	
1370			898		898
		1323	814		
1306m	1303m	1307m	761m }		755m
		1297	755 }		
1286		1285	742m	742s	
1266		1267m			725
1242		1242m			685
		1227	672	672	
1219			652	651	
1212		1212m	626		627

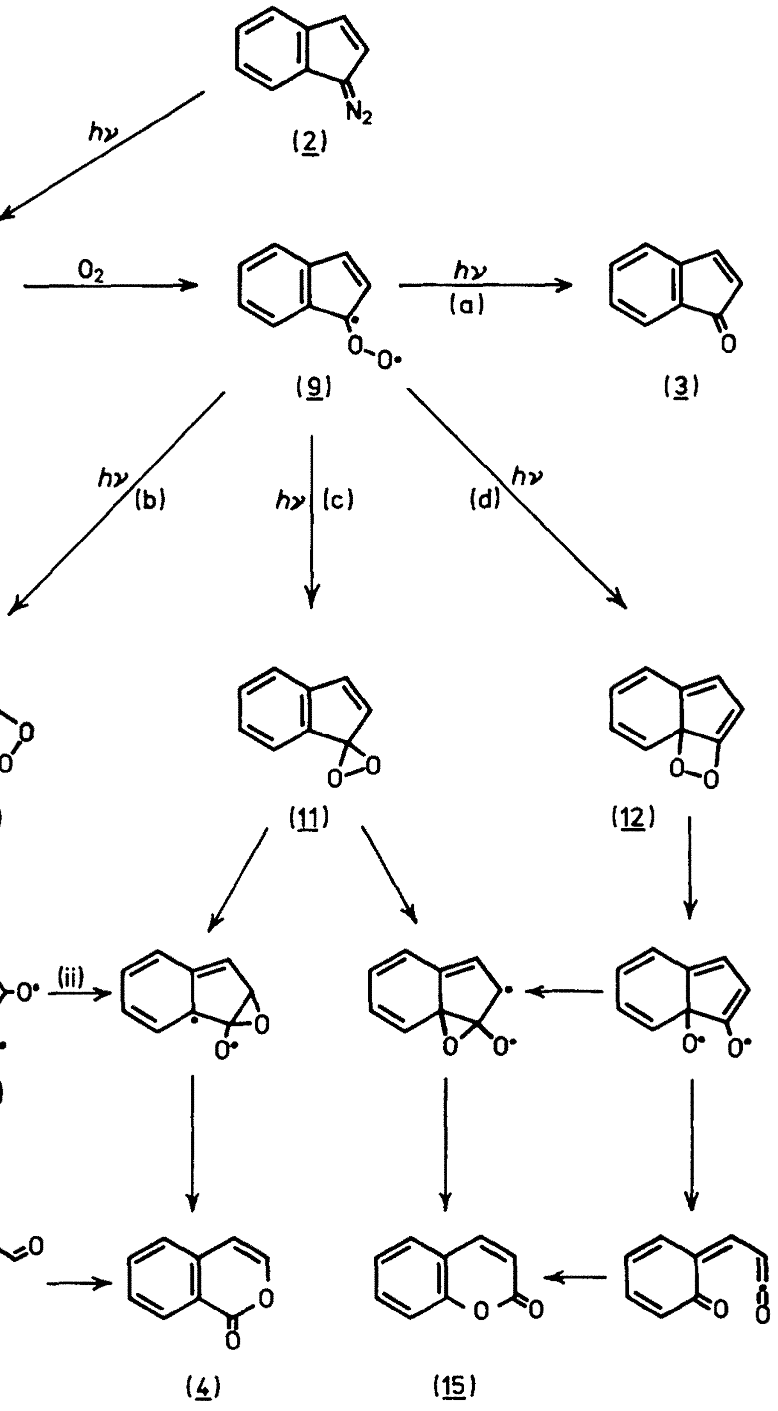
†Qualitative band intensities: bands were weak unless denoted s (strong) or m (medium).

DISCUSSION

Photo-oxidation of diazoindene (2).- Wide-band photolysis of (2) in O_2-doped matrices yields indenone (3) and isocoumarin (4), with only traces of other products [Scheme 1]. More discriminating photolysis (λ = 312 ± 5nm), however, allows the detection of a highly photolabile precursor of (3) and (4), and we identify this intermediate species as indenone O-oxide (9). The following evidence supports this assignment. Firstly, the intermediate is almost certainly an adduct of indenylidene (8) and O_2. Matrix photolysis of (2) in the absence of O_2 is known to give (8),[11] and the intermediate seems to arise when matrices containing both (8) and O_2 are annealed. Secondly, the formation of (4) on wide-band photolysis of the intermediate favours a structure containing two oxygen atoms. Thirdly, the mode of formation of the intermediate and its subsequent photolysis are closely similar to the chemistry of cyclopentadienone O-oxide reported previously.[5,10] Fourthly, u.v.-visible studies have already demonstrated that (8) and O_2 react in matrices to give a highly photolabile species with λ_{max} = 445 nm, which is also identified as (9).[6]

The photochemistry of carbonyl oxides of this type has been discussed in connection with cyclopentadienone O-oxide, and several plausible reaction pathways have been proposed.[10,19] A slightly simplified adaptation of the various proposals to indenone O-oxide is given in Scheme 3. One of the observed products, indenone (3), arises by simple ejection of an oxygen atom from (9) [path (a)], although so far we have been unable to determine the fate of

Scheme 3.



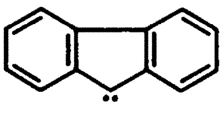
the ejected atom. The other product, isocoumarin (4), is an isomer of (9). A number of rearrangement pathways may be written for (9), but the exact route followed remains to be verified. Nevertheless, arguments can be advanced[10] which favour initial formation of a dioxetane (10) [path (b)], followed by O-O bond-cleavage and ring-opening [path (i)], to give the ketene-aldehyde(14). Final electrocyclic ring-closure would result in the observed product (4). An alternative route from the diradical (13) to (4) [path (ii)] is also possible.

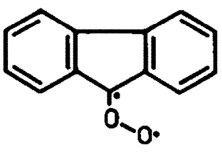
Rearrangement of (9) *via* dioxirane (11) [path (c)] should also be considered, especially since an analogous photodecomposition route for a thione *S*-oxide has been put forward.[20] The dioxetane route [path (b)], however, would have the more highly delocalised transition state, and this has been taken to favour path (b) over path (c).[10]

A second dioxetane pathway [path (d)] can be ruled out for the photo-oxidation of (2), because it would lead *via* (12) to coumarin (15), which was not detected as a product of the reaction. The attack of the terminal oxygen at the bridgehead position in (9) might, in any case, seem unlikely on steric grounds, but such attack apparently occurs quite readily in fluorene *O*-oxide (17) (see below). A conformational preference of (9) to have the terminal O-atom away from the benzene ring may be all that is required to favour path (b) over path (d).

Finally, it is worth emphasizing that of all the possible intermediates that lie on the route between (2) and (4), only the carbene (8) and the carbonyl oxide (9) have been directly detected. Specially noteworthy is that we have not detected ketene-aldehyde (14) [ν(CCO) ca. 2130 cm^{-1}] in our experiments, even though the analogue in the reaction of cyclopentadienone *O*-oxide is well known, and exists in photo-equilibrium with α-pyrone.[10,19,21] Failure to detect (14) cannot, however, be taken as reliable evidence against its intermediacy. With rearomatization of the benzene ring as an important part of the driving force, ring-closure of (14) to give (4) is likely to be very efficient.

Photo-oxidation of diazofluorene (5).- The photo-oxidation of (5) in O_2-doped matrices proceeded in a similar manner to that of (2), and much of the discussion in the previous section applies, *mutatis mutandis*. Wide-band irradiation of (5) in O_2-doped matrices gave fluorenone (6) and dibenzopyran-6-one (7) [Scheme 2]. Narrow-band irradiation ($\lambda = 312 \pm 5$ nm), however, permitted the observation of a very photolabile intermediate, to which we assign the carbonyl oxide structure (17). Fluorenone *O*-oxide (17) has been detected before by u.v.-visible spectroscopy, both as an adduct of O_2 and fluorenylidene (16) in N_2 matrices ($\lambda_{max} =$ 460 nm),[6] and as a transient species in flash photolysis studies,[9] but no previous report of its i.r. spectrum has been made. A Scheme similar to that shown for (9) may also be drawn for the photolysis of (17). Photo-ejection of an oxygen atom from (17) leads to fluorenone (6), while dibenzopyran-6-one (7) could be derived *via* a dioxetane or a dioxirane, with the former more probable. As with (9), we observed no ketene intermediate in the photolysis of (17), but this does not rule out the intervention of such a species.


(16)



(17)

Structure and bonding in carbonyl oxides.- I.r. studies exploiting isotopically labelled oxygen have shown that the adduct of O_2 with cyclopentadienylidene has two non-equivalent oxygen atoms, thus excluding a dioxirane structure for this molecule.[5] It is reasonably safe to assume that the oxygen atoms in the adducts of (8) and (16) with O_2 will be similarly disposed.

The rather small variation in the positions of the electronic absorptions of the adducts of O_2 with cyclopentadienylidene (λ_{max} = 410 nm),[6] indenylidene (λ_{max} = 445 nm),[6] fluorenylidene (λ_{max} = 460 nm),[6] diphenylcarbene (λ_{max} = 410 nm),[8] and 10,10-dimethyl-10-sila-anthracen-9[10H]-ylidene (λ_{max} = 425 nm)[7] also tends to favour carbonyl oxide structures [e.g. (9) and (17)] rather than dioxetane structures [e.g. (10)], since the latter would be expected to exhibit strong polyene absorptions dependent on the carbocyclic skeleton.

Ab initio[22] and MINDO/3 calculations[3e,23] on simple carbonyl oxides agree that the ground states of these species should be singlets, and generally favour a zwitterionic description of the bonding [cf. (1b) and (1c)]. For the least substituted examples [e.g. (1, R=H)], however, the ab initio calculations prefer a biradical description [cf. (1a)]. Experimental evidence relating to the singlet character of the ground states and the biradical or zwitterionic nature of the bonding is rather sparse. The i.r. spectra of cyclopentadienone O-oxide and its ^{18}O-labelled analogues do not seem compatible with a structure having substantial double bond character between the ring-carbon and oxygen.[5,24] The i.r. spectra of (9) and (17) do not provide any contrary evidence, but add little new to this conclusion. Thus, the inference from i.r. spectroscopy is against a substantial contribution from structure (1b) to the bonding in carbonyl oxides of this type, but leaves biradical [cf. (1a)] and ylide-type zwitterionic [cf. (1c)] bonding schemes, or a resonance hybrid of the two, as plausible options. Some authors have sought to deduce from the u.v-visible spectrum of a carbonyl oxide that the biradical structure is preferable,[7] but our view is that the electronic absorptions are unlikely to provide a simple and reliable means of deciding this issue.[6]

On the question of the spin states of carbonyl oxides we can now be more definite. It is known from e.s.r. studies that both indenylidene (8) and fluorenylidene (16) have triplet ground states.[25] Both of these carbenes react with CO in low-temperature matrices to give the corresponding ketenes.[11] This is an interesting reaction, since because both CO and the ketenes are singlets, an electronic spin-inversion must occur at some point on the pathway. It was found that the reactivity of (8) and (16) towards CO is somewhat limited. Both carbenes can be generated in pure CO matrices at 12K, and seem to be able to exist in these conditions more or less indefinitely. Only upon warming the matrices to about 30K does the thermal ketene-forming addition take place at a reasonable rate. We have previously suggested that the rate-limiting factor in the reaction of (8) or (16) with CO may be steric in origin or may be the result of the necessary spin-inversion.[11] The first of these possibilities now seems much less likely, owing to the very facile reaction between (8) or (16) and O_2. It has proved very difficult to generate detectable concentrations of these carbenes in matrices containing even as little as 0.1% O_2, a fact which made the i.r. observation of the formation of (9) and (17) in annealing experiments rather marginal. There is, therefore, a great difference in the reactivity of (8) and (16) towards CO, on the one hand, and O_2 on the other. Such a reactivity difference makes little sense in the context of arguments based on steric effects, but fits in well with rate-limitation due to spin-inversion. Thus, taking the simplest view, we propose that the reaction between a triplet carbene and triplet ground state O_2 to give a triplet carbonyl oxide would involve a rate-limiting electronic spin-inversion, whereas the formation of a singlet carbonyl oxide would not. The high reactivity of (8) and (16) towards O_2 may therefore be interpreted as evidence in favour of singlet ground states for (9) and (17), as predicted by theory.[3e,22,23]

CONCLUSIONS

This investigation was an i.r. study of the photolysis of diazoindene (2) and diazofluorene (5) in low-temperature matrices containing O_2. Under these conditions, the carbenes, indenylidene (8) and fluorenylidene (16), react with O_2 to give the corresponding carbonyl oxides, (9) and (17), respectively. Matrix i.r. spectra for these species are reported. Subsequent photolysis of the carbonyl oxides follows two routes: (i) the ejection of an oxygen atom, yielding ketones (3) or (6), and (ii) an isomerization, yielding lactones (4) or (7). Mechanisms for the photo-isomerization of carbonyl oxides (9) and (17), based on earlier proposals for cyclopentadienone O-oxide, are discussed, and some attempt is made to decide between the various possible routes. The nature of the bonding in carbonyl oxides is also discussed, and evidence based on the reactivity of (8) and (16) towards O_2 and CO is taken to favour singlet ground states for carbonyl oxides (9) and (17), as predicted by published theoretical studies.

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