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PHOTOLYSIS OF POLYFLUOROTRIARYLNITRONES. THE STABLE TRIARYLOXAZIRIDINES*

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SUMMARY

Photoisomerization of polyfluorinated triarylnitrones has been investigated. This reaction can be used for the preparation of the stable polyfluorotriaryloxaziridines.

INTRODUCTION

Irradiation of nitrones generally results in cyclization to the isomeric oxaziridines. The stability of the latter depends on the nature of the substituents, with the strongest effect produced by substituents on nitrogen. Oxaziridines with an aryl group in the 2 position are much less stable than 2-alkyloxaziridines, and in general, compounds with aryl substituents in both the 2 and 3 position are too unstable, either thermally or to light, to be isolated [2,3]. It has been found [4,5] that triphenyloxaziridine is relatively stable although no analytical data have been reported on this compound. In this paper photolysis of polyfluorinated triarylnitrones has been investigated.

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*A part of this material was published earlier as a short communication [1].

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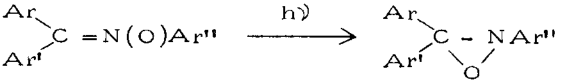
RESULTS AND DISCUSSION

Irradiation with a 500 W high pressure mercury lamp of polyfluorinated triarylnitrones of the type I in organic solvents (ethanol, ether, benzene, n-hexane) or in the solid state gave polyfluorotriaryloxaziridines (II) in high yields.



I a-d II a-d 70-95%

a, $Ar=Ar'=C_6F_5$; $Ar''=Ph$
b, $Ar=Ar'=Ph$; $Ar''=C_6F_5$
c, $Ar=Ph$; $Ar'=Ar''=C_6F_5$
d, $Ar=Ar'=Ar''=C_6F_5$

As with their non-fluorinated analogues, these compounds liberated iodine from acidic potassium iodide and had UV-absorptions at much shorter wave length than the corresponding nitrones. Their structure has been confirmed by data from elemental analysis, molecular weights determined mass spectrometrically, and their ^{19}F NMR spectra.

There has been some evidence for the stereospecific formation of oxaziridines from nitrones [6-8]. However, the character of the ^{19}F NMR spectrum of compound (II c), prepared from a mixture of E- and Z-isomers of nitrone (I c), indicated either the existence of a single isomeric species or, less probably, rapid nitrogen inversion.

The photoisomerization of compounds (I a-d) was investigated quantitatively and compared with that of α,N-diphenyl-α-pentafluorophenylnitrone (III) and triphenylnitrone (IV). The quantum yields were calculated from the ratio of the decrease in the number of nitrone molecules to the number of quanta absorbed by the nitrone. It was assumed that the quantum yields of disapearance of nitrones were equal to those of oxaziridines formation because the UV spectral changes showed isobestic points as shown in Fig.1. The first absorption bands of nitrones and the quantum yields of nitrone isomerization to oxaziridine are summarized in Table 1. The results indicate that the quantum efficiency of this process does not depend on the presence of fluorine atoms in the molecule of starting nitrone.

Triaryloxaziridines of the type II, prepared by photolysis of the corresponding nitrones, can be chromatographed on SiO_2 and recrystallised from ethanol; they have sharp melting points and are stable for a long time in the absence of direct sunlight. Their non-fluorinated analogue, obtained from nitrone (IV), melts within a wide temperature range ($120-170^{\circ}$) and contains a mixture of benzophenone and N,N-diphenylbenzamide as shown by IR-spectra and chromatography on SiO_2. We have not succeeded in isolating 2,3-diphenyl-3-pentafluorophenyloxaziridine in its individual form from the product of photolysis of nitrone (III) since it became transformed into 2,3,4,5,6-pentafluorobenzophenone.

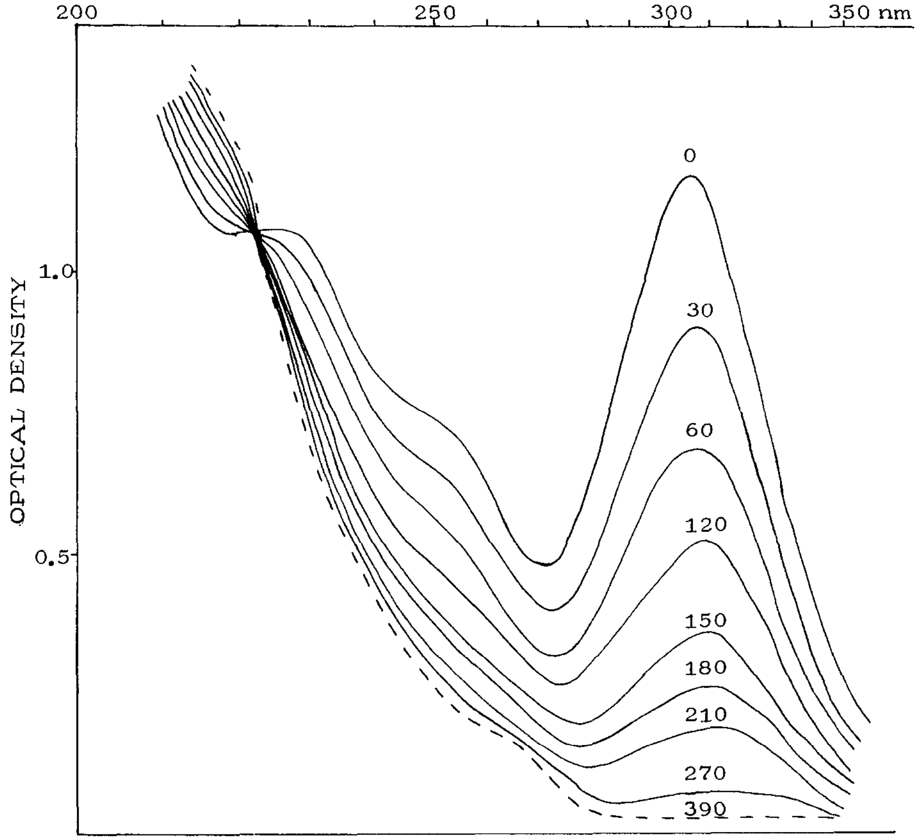


Fig.1. The progressive decrease of the spectrum of nitrone (I b) on 314 nm irradiation. Numbers refer to time of irradiation in seconds, and dotted line denotes a spectrum of oxaziridine (IIb).

TABLE 1

The first absorption bands and quantum yields of photoisomerization for triarylnitrones and the half-times of decomposition for corresponding oxaziridines

Nitrone	λ_{max}, nm	φ^{*}_{314}	$\tau_{1/2}$, s
Ia	288	0.46	160
Ib	314	0.26	200
Ic	310	0.29	
Id	290	0.40	120
III	304	0.31	
IV	312	0.34	170

*Relative error $\leq$ 10%.

It is known that ketone and amide products can be obtained by thermal or photochemical transformations of oxaziridines [2]. In order to get some information on the relative photochemical activity of triaryloxaziridines, the half-times of their decompositions at 253 nm light irradiation were calculated by measuring the optical absorption of reaction products (see Fig. 2). From the obtained data shown in Table 1, it is clear that the rate of photochemical decomposition of polyfluorotriaryloxaziridines is similar to that of the non-fluorinated analogue. It is obvious that the stability of compounds of type II is due to their thermal inactivity. This seems to be the result of the lesser stabilization of the developing nitrogen cation from N-O bond cleavage by the strongly electron-withdrawing C_6F_5 groups.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a "Varian A 56/60A" spectrometer at the frequency of 56.4 MHz for solutions in THF. Internal standard was hexafluorobenzene.

Materials

Initial polyfluorinated triarylnitrones were prepared by published methods [9, 10], as was triphenylnitrone (IV) [11]. Ether was dried over calcium chloride; other solvents were reagent grade products.

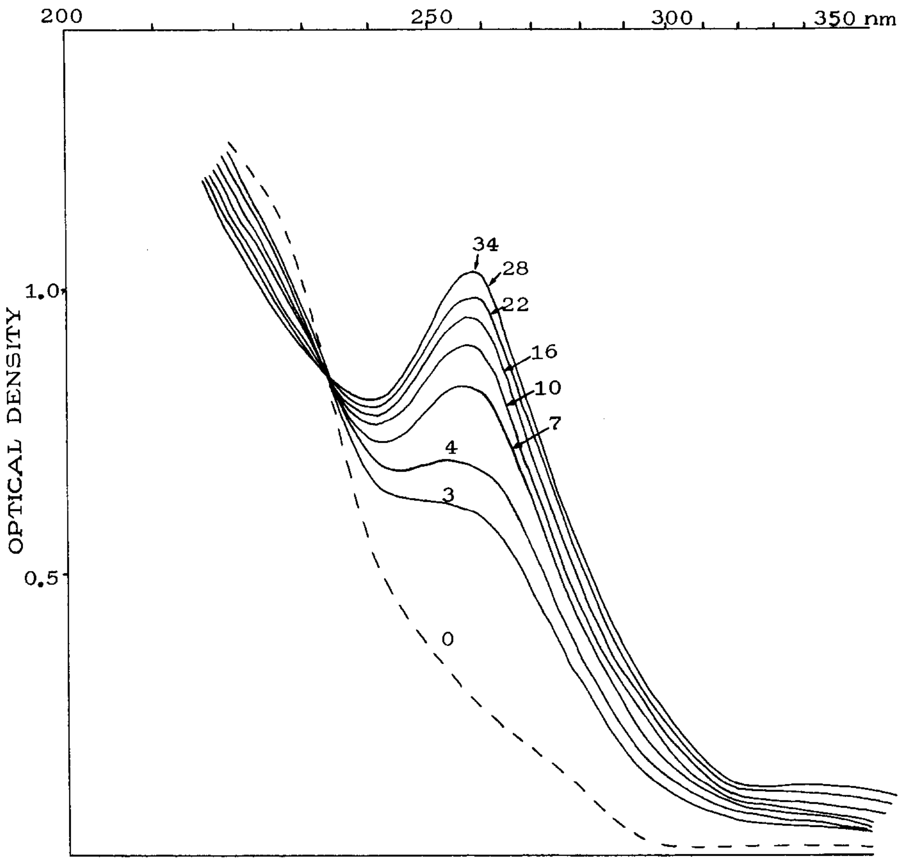


Fig.2. Spectral change of the oxaziridine (IIb) in ethanol on 253 nm irradiation. Numbers refer to time at measurement in minutes.

Irradiation of triarylnitrones (I)

A 1×10^{-2}M solution of nitrone (I) was irradiated with a 500 W high pressure mercury lamp for 1+1.5 h at 25-30°C in an air-cooled Pyrex tube 2 cm thick, 30 cm distant from light source. The product was obtained by evaporation of solvent and treatment the residue with ethanol. All the oxaziridines prepared in this study are new compounds and are listed in Table 2 with their melting points, elemental analysis and data of ^{19}F NMR spectra.

TABLE 2

Polyfluorotriaryloxaziridines, prepared by photolysis of corresponding nitrones in ether

Compound	Yield, %	M.p., °C (of ethanol)	Formula	Calcd, % / Found, % C	 H	 F	 N	^{19}F NMR spectrum, δ, p.p.m. (intensity ratio)
II a	95	143-145	$C_{19}H_5F_{10}NO$	50.35 50.51	1.11 1.15	41.92 41.69	3.09 3.07	1.6, 11.3, 12.9, 23.6, 25.9 (2 : 2 : 1 : 1 : 4)
II b	84	103-105	$C_{19}H_{10}F_5NO$	62.82 62.80	2.77 2.81	26.15 25.98	3.85 3.63	-0.5, 2.9, 14.7 (2 : 1 : 2)
II c	70	89-91	$C_{19}H_5F_{10}NO$	50.35 50.14	1.11 1.41	41.92 41.47	3.09 3.02	0.0, 1.4, 4.9, 10.6, 16.8, 22.8 (2 : 2 : 1 : 1 : 2 : 2)
II d	90	120-121	$C_{19}F_{15}NO$	42.01 41.83		52.47 52.50	2.58 2.65	1.6, 2.8, 7.0, 12.2, 15.8, 24.2, 26.3 (2 : 2 : 3 : 1 : 1 : 2 : 4)

For irradiation in the solid state, a thin film of powder of the starting nitrone (0.2 g) was placed between glass plates (9×12 cm^{-2}), 50 cm distant from light source.

Quantum yields determination

The quantum yields of the nitrones photoisomerization were obtained by measuring the decrease of the starting compound absorption on irradiation of 1×10^{-4} M ethanol solution in quartz cell. A high pressure mercury lamp equipped with monochromator MDR-2 ($I = 2.45 \times 10^{-9}$ Einstein/s) was used for 314 nm radiation source. The intensity of the incident light was measured periodically by the ferrioxalate actinometric method. Change in UV spectrum caused by irradiating was recorded on a "Specord UV-VIS" spectrometer.

The half-times of photochemical decompositions of triaryloxaziridines determination

1×10^{-4}M solution of oxaziridine in ethanol obtained by photolysis of corresponding nitrone, was irradiated at 253 nm with a 1000 W high pressure xenon lamp equipped with an interference filter ($I = 5 \times 10^{-9}$ Einstein/s). The half-times of decomposition of oxaziridines were calculated from spectral change recorded on a 'Specord UV-VIS' spectrometer.

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