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ABSENCE OF TRIAZIRINE INTERMEDIATES IN THE PHOTOLYTIC FORMATION OF AZIDES FROM MESOIONIC 3-SUBSTITUTED 1,2,3,4-OXATRIAZOLYLIO-5-OXIDES

ISOTOPE LABELLING EXPERIMENTS

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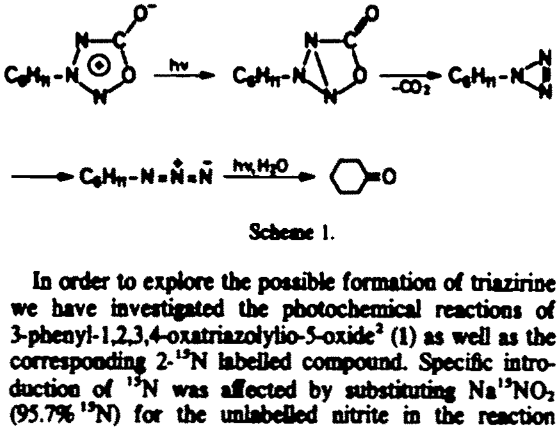
Abstract—Irradiation of 3-phenyl-1,2,3,4-oxatriazolylio-5-oxide (1) leads to formation of CO_2, N_2O, phenyl azide and phenyl isocyanate. The two latter compounds are observed only in low yields because of secondary photolytic reactions. Photolysis in CCl_4 or $Cl_2C{=}CCl_2$ of 2-^{15}N labelled (1) leads almost exclusively to the formation of 3-^{15}N labelled phenyl azide identified by IR spectroscopy on comparison with authentic 1-^{15}N, 2-^{15}N and 3-^{15}N labelled phenyl azides, respectively. These results show that phenyl azide is formed photolytically from (1) via phenyl migration and not via "antiaromatic", phenyl triazirine (2).

Triazirine, the so-called antiaromatic isomer of the azide group has never been isolated or characterized. Cyclohexyl triazirine was suggested as an intermediate in the photochemical formation of cyclohexanone (27%) from 3-cyclohexyl-1,2,3,4-oxatriazolylio-5-oxide.[1] Kato *et al.*[1] did not isolate other products from the reaction, but proposed cyclohexyl azide as an intermediate (Scheme 1).



Scheme 1.

In order to explore the possible formation of triazirine we have investigated the photochemical reactions of 3-phenyl-1,2,3,4-oxatriazolylio-5-oxide[2] (1) as well as the corresponding 2-^{15}N labelled compound. Specific introduction of ^{15}N was affected by substituting $Na^{15}NO_2$ (95.7% ^{15}N) for the unlabelled nitrite in the reaction sequence[3] (eqn 1). In agreement herewith the mass spectrum shows loss of ^{15}NO from the molecular ion (Experimental).

1

RESULTS AND DISCUSSION

Irradiation of 1 (0,02 M, CCl_4, N_2) resulted in a 66% yield of CO_2 ($BaCO_3$). Monitoring of the photolysis ($\lambda = 300 \pm 20$ nm) in CCl_4 or $Cl_2C = CCl_2$ (0,1 M) by means of IR spectroscopy (2500–2000 cm^{-1} region) revealed the appearance of absorption bands at 2330, *ca.* 2267, 2220, 2130 and 2100 cm^{-1} (Fig. 1) assigned to CO_2 (2349 cm^{-1}),[4] phenyl isocyanate (doublet, 2278, 2260 cm^{-1}),[5,6] N_2O (2224)[4] and phenyl azide (2129 and 2100).[7a] Continued irradiation resulted in reduction of the intensity of the bands assigned to phenyl azide.

Formation of phenyl azide (2%) and phenyl isocyanate (1%) was substantiated by glc/ms and the gas chromatogram further showed the presence of a compound which was identified as chlorobenzene (18%). The phenyl isocyanate gave rise to N,N'-diphenylurea on reaction with aniline and it was shown that phenyl isocyanate is not a photolysis product from the reaction of phenyl azide with CO_2 under the experimental conditions used. The formation of chlorobenzene was not further investigated.

The low yield of phenyl azide is somewhat surprising compared to the amount (66%) of CO_2 formed. However, phenyl azide absorbs at about 285 nm,[8] which is close to the absorption of 1 ($\lambda_{max} = 267$ nm, C_2H_5OH) and is therefore undergoing photolysis mainly with formation of tar.[9,10] In the present case tlc indicates that the same tar is formed on photolysis of authentic phenyl azide (in CCl_4) and of 1 (CCl_4).

The results so far described indicate that two fragmentation processes are operating on photolysis of 1. One leading to phenyl azide and CO_2 and the other to phenyl isocyanate and N_2O. The former process is clearly the dominating under the conditions employed (Scheme 2).

Photolysis of 2-^{15}N-3-phenyl-1,2,3,4-oxatriazolylio-5-oxide was monitored by IR spectroscopy as described for the unlabelled compound. Bands were observed at ~2322 (1), 2270 (2), 2218 (3), 2196 (4), 2171 (5), 2149 (6), 2114 (7) and 2069 (8) cm^{-1} (Fig. 2a). On leaving the

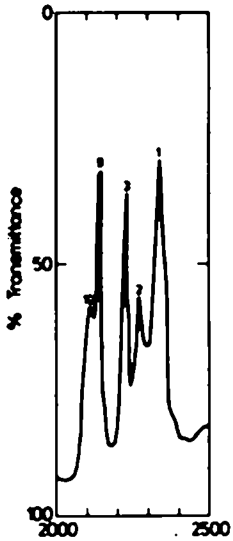
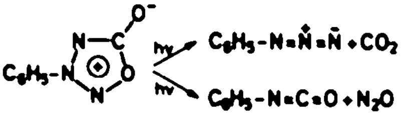


Fig. 1. IR spectrum in the 2000–2500 cm^{-1} region of the photolysis products from 1 in CCl_4.



(1)

Scheme 2.

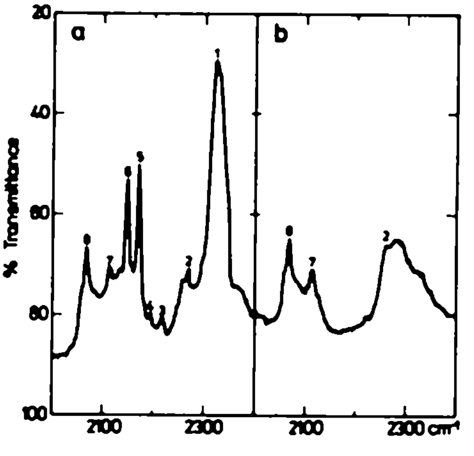
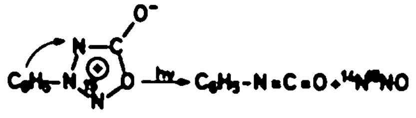


Fig. 2. IR spectra in the region 2000–2400 cm^{-1} of the photolyses products from 2-^{15}N labelled 1 in CCl_4. (a) recorded immediately after irradiation, (b) the same mixture after 24 hr storage in the dark.

solution at −20° in the dark for 24 hr bands 1,3,4,5 and 6 disappeared (Fig. 2b). As above band 1 is assigned to CO_2 and band 2 to phenyl isocyanate. The bands 3,4,5 and 6 are assigned to $^{14}N^{14}NO$, $^{15}N^{14}NO$, $^{14}N^{15}NO$, and $^{15}N^{15}NO$, respectively. The reported gas phase values for these absorptions are 2223.9, 2202.5, 2177.6 and 2156.2 cm^{-1},[11] which is consistently 6 cm^{-1} at higher frequency, undoubtedly due to the different media.

The presence of $^{14}N^{15}NO$ is accounted for in the photolysis leading to phenyl isocyanate (eqn 2).



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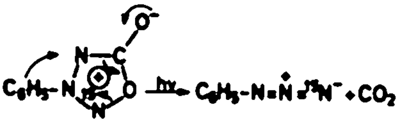
Comparison with the authentic 1-^{15}N, 2-^{15}N and 3-^{15}N labelled phenyl azide,[7] see Figs. 3(b), (c) and (d), prompt us to assign band 7 and 8 (Fig. 2a) to 3-^{15}N phenyl azide. These results can only be interpreted to mean that phenyl azide is formed, in the main reaction pathway, by phenyl migration and not via a triazirine.



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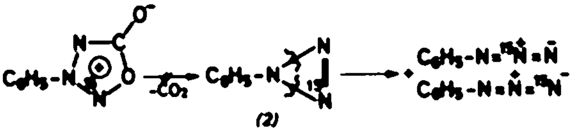
If phenyl triazirine (2) was an intermediate it must be generated with ^{15}N at position 2. On decomposition equal amounts of 2-^{15}N and 3-^{15}N labelled phenyl azide must be formed[12] (Scheme 3).



(2)

Scheme 3.

Whether the processes depicted in eqn (2) and (3) are concerted reactions or whether 4-phenyl-1,2,3,4-oxatriazolin-5-one is a discrete but thermally or photochemically unstable intermediate is at present unknown.

Formation of $^{15}N^{15}NO$ and $^{15}N^{14}NO$ is not accounted for but is clearly not the result of nitrogen scrambling in 1 during irradiation as evidenced by the formation of only 3-^{15}N phenyl azide. Other reaction paths, e.g. ring opening[13] may account for these unexpected products.

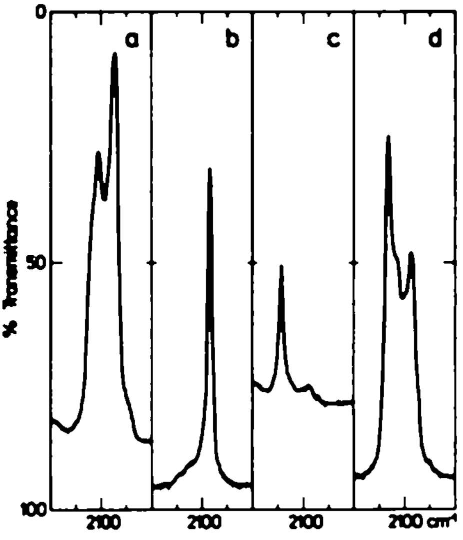


Fig. 3. IR spectra in the region 2000–2200 cm^{-1} of dilute solns of phenyl azide and ^{15}N substituted phenyl azides in CCl_4. The cell thickness is 0.1 mm and concentrations used are not equal (Experimental). (a) parent, (b) 1-^{15}N, (c) 2-^{15}N and (d) 3-^{15}N.

EXPERIMENTAL

Routine IR spectra were recorded on a Perkin Elmer spectrophotometer model 337 while the IR spectra used for identification of the isotopically labelled species were recorded on a Perkin Elmer spectrophotometer model 125. In no cases were the instruments purged with gases to prevent absorption from atmospheric CO_2 therefore the intensity and exact position of the CO_2 band (1 in Fig. 2) may be a little erronious. The IR spectra of phenyl azide and isotopic species dissolved in CCl_4, were recorded using a KBr liquid cell with 0,1 mm spacing. To save compound the solns were made by dissolving a small amount taken on a spatula in 1 ml CCl_4. This procedure is of course not quantitative, therefore the relative insensities of the absorption bands of the individual isotopic species do not appear from the spectra shown in Fig. 3.

3-Phenyl-1,2,3,4-oxatriazolylio-5-oxide (1) was synthezised by a slightly modified literature procedure.[3] The 2-^{15}N labelled compound was obtained by the same synthesis only $Na^{15}NO_2$ 95.7% ^{15}N was substituted for $NaNO_2$ in the last reaction as outlined in eqn (1). The absorption spectrum exhibited two maxima at $\lambda = 267$ nm, $\epsilon = 9.6 \times 10^3$ and $\lambda = 217$ nm, $\epsilon = 6.5 \times 10^3$. The exact location of the ^{15}N label was secured by comparison between the mass spectra of the labelled and unlabelled compounds. Base peak in the two spectra were *m/e* 77 (100%). The molecular ions for the ^{14}N and ^{15}N compounds (*m/e* 163 and 164 respectively) looses ^{14}NO and ^{15}NO giving rise to *m/e* 133 (22%) and *m/e* (32%) respectively.

Photolysis of 1 *in* CCl_4 *and* $Cl_2C{=}CCl_2$. Photolysis ($\lambda \geq$ 300 nm) of a soln of 1 (72.2 mg) in CCl_4 (20 ml) for 3 hr followed by reisolation of unreacted 1 (26 mg) resulted in a yield of 66% CO_2. The yield was calculated on basis of transformed 1 and determined by continuous removing of CO_2 by a flow of N_2, which gave rise to $BaCO_3$ (39 mg) on contact with a saturated $Ba(OH)_2$ soln.

Irradiation ($\lambda = 300 \pm 20$ nm) of 0.1 M soln of 1 in CCl_4 or in $Cl_2C{=}CCl_2$ was carried out in a KBr IR cell with a spacing of 1.0 mm allowing the reaction to be monitored directly by IR spectroscopy. The resulting spectra, which is described and shown in this paper (results and discussion) were recorded at room temp. as was the irradiation. In order to secure the thermal stability of 1 during the photolysis an identical unexposed soln was kept at 60° during 1 hr without any change in the IR spectrum of the chromatogram.

A photolysis of 1 (0.1 M) in CCl_4, conducted as the one mentioned under the CO_2 estimation above, was monitored by tlc. Silica gel tlc with a mixture of petrol ether: benzene: ethylether, 3:2:1 as eluent showed spots coinciding with authentic phenyl azide and with phenyl isocyanate. Furthermore, after addition of aniline the spot assigned to phenyl isocyanate disappeared and a new spot with identical retention value as that of authentic diphenylurea appeared. Glc (10% SE 30, 90°) analysis of the mixture showed peaks with identical retention volumes as phenyl azide and phenyl isocyanate. Phenyl isocyanate was found in low concentration, while one of two major peaks were phenyl azide and the other proved to be chlorobenzene, identified by glc–ms. A trace compound was unidentified.

During the photolysis the soln turns reddish and a solid substance starts to precipitate. Exactly the same could be observed when authentic phenyl azide was subjected to the same photolytical conditions. Tlc analysis (petrol ether: benzene: ethanol, 2:2:1) showed identical pattern of the product distribution from the two experiments except the fact that phenyl isocyanate is not formed in the latter reaction. The presence of chlorobenzene was noted in the phenyl azide photolyses. We therefore conclude that at least some of the reddish colour (giving rise to a tar on attempted isolation), chlorobenzene, and the ppt in fact originates from secondary photolysis of phenyl azide.

The glc experiments allowed estimation of the yields of chlorobenzene (18%), phenyl azide (~2%), and phenyl isocyanate (<1%) based on reacted 1 (bromobenzene was used as an internal standard). From the phenyl azide photolysis experiment chlorobenzene was present in a yield <1%.

The photolysis of the labelled compound (22 mg) was performed directly in a KBr cell (1,0 mm spacing) in CCl_4 (1,0 ml) as described above for the unlabelled compound. IR spectra were recorded after 0.5, 1 and 2 hr. The results are described in section: results and discussion.

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