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PHOTOCHEMICAL GENERATION OF KETENES. AN ULTRA-VIOLET AND INFRA-RED SPECTROSCOPIC STUDY OF 1- AND 2-DIAZONAPHTHALENONES AT 77K.

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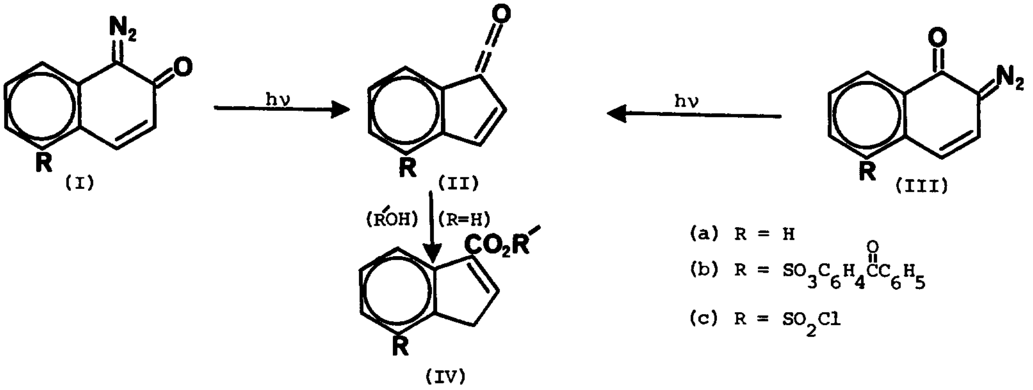
ABSTRACT. Direct photolysis of 1- or 2-diazonaphthalenone and 2-diazonaphthalenone-5-sulfonyl chloride at 77K yields the respective indenoketenes which were identified by ultra-violet and infra-red spectroscopy.

INTRODUCTION. The chemistry of 2-diazoketones has attracted much interest because of their ability to undergo the Wolff rearrangement upon thermolysis or photolysis.[1] The photochemistry of 1- and 2-diazonaphthalenones is particularly important industrially due to their application as positive photoresists in polymer films.[2] Photolysis and thermolysis of 1- and 2-diazonaphthalenones (I and IIIa) in solution results mainly in products derived from 1-indenoketene (IIa) which is formed by the Wolff rearrangement of the diazoketone.[3,4] 1-Indenoketene may be trapped with alcohols to give the ester derivatives of indene-3-carboxylic acid, which could be formed by isomerization of the indene-1-carboxylic acid derivative,[4] or directly from the ketene.[5] Recently, the photolysis of a substituted 2-diazonaphthalenone (IIIb) was studied by infra-red spectroscopy at 77K, and the ketene (IIb) was proposed for the intermediate.[6] A similar reaction was also observed at 8K for the same compound upon exposure to an electron beam.[7]

We report here an ultra-violet (UV) and infra-red (IR) absorption spectroscopic study at 77K of the photolysis of the unsubstituted 1- and 2-diazonaphthalenones (I and IIIa) and of 2-diazonaphthalenone-5-sulfonyl chloride (IIIc).

RESULTS AND DISCUSSION. 1-Diazonaphthalenone and 2-diazonaphthalenone-5-sulfonyl chloride were prepared by literature methods.[8,9] Since the route described in the literature for the synthesis of 2-diazonaphthalenone is rather lengthy, the method for the preparation of 9,10-diazophenanthrenone was modified.[10] Treatment of 1,2-naphthoquinone (10 mmole) with p-toluenesulfonyl hydrazine (10 mmole) in dichloromethane at 0°C and stirring for 5 hours, resulted in a deep red solution. Chromatography of this solution on a dry alumina column,[11] followed by elution with dichloromethane, gave a quantitative yield of the diazoketone, which was further purified by recrystallization from hexanes (m.p. 75-77°C, lit.[8] 77°C) and stored at 0°C.

The UV absorption spectrum of compound I exhibits temperature dependence on cooling (Figure 1). The bands below 300 nm show a loss of fine structure and intensity at 77K, whereas the bands above 300 nm show an increase in intensity and are red shifted. This red shift can be seen visually; cooling a solution of compound I results in a deeper yellow coloration, which disappears when warmed to room temperature. Upon irradiation at 77K (Ealing 200W Hg lamp ; 340 nm cut-off filter), the matrix turns from yellow to colorless and the UV absorption spectrum shows new bands at 310 nm (ε 5.39 x 10^3 M^{-1} cm^{-1}) and 250 nm (ε 1.63 x 10^4 M^{-1} cm^{-1}), and simultaneous loss of the absorptions due to starting material. These new bands (∿310 and 250 nm) disappear when the sample is warmed to room temperature and re-cooled to 77K (annealing). The



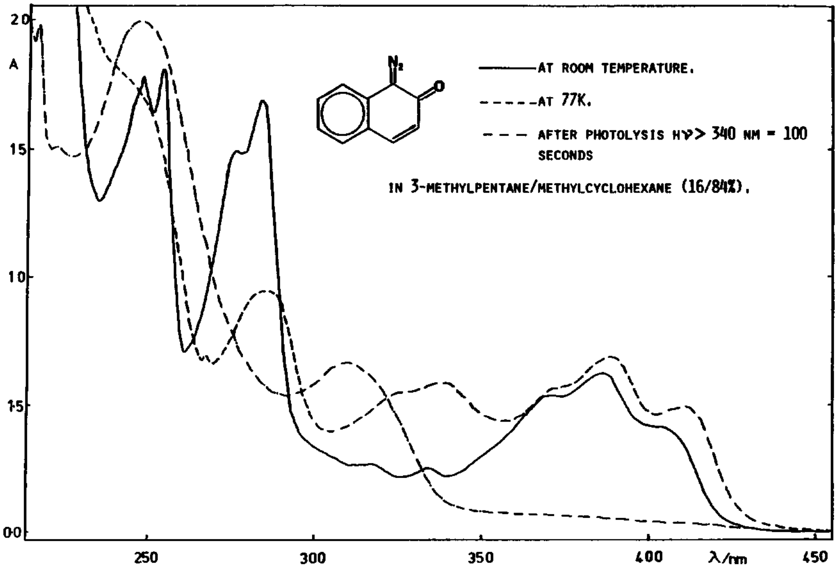
(a) R = H

(b) R = $SO_3C_6H_4\overset{O}{\overset{\|}{C}}C_6H_5$

(c) R = SO_2Cl

isomeric diazonaphthalenone (IIIa) also shows a red shift for its absorption bands above 300 nm upon cooling to 77K (Figure 2). Irradiation of this compound at 77K also results in new absorption bands at 310 nm and 250 nm (ε 5.42 x 10^3 M^{-1} cm^{-1} and 2.76 x 10^4 M^{-1} cm^{-1}, respectively),

FIGURE 1 ULTRA-VIOLET SPECTRA OF 1-DIAZONAPHTHALENONE



which disappear after annealing (spectrum not shown). From these experiments, a common intermediate is deduced to be generated in the photolysis of Ia or IIIa at 77K and is assigned the structure IIa.[12]

Experiments using IR absorption spectroscopy at 77K were also performed with the aim of confirming the structure of the ketene intermediate (II). 2-Diazonaphthalenone (IIIa) was sublimed onto a sodium chloride window at 77K under vacuum and its IR spectrum recorded (Figure 3). The spectrum showed peaks at 2152 cm^{-1} and 2122 cm^{-1} (CN_2 stretch) and 1615 cm^{-1} (C=O stretch), typical for a diazoketone structure[13], and a series of peaks below 1600 cm^{-1}. Irradia-

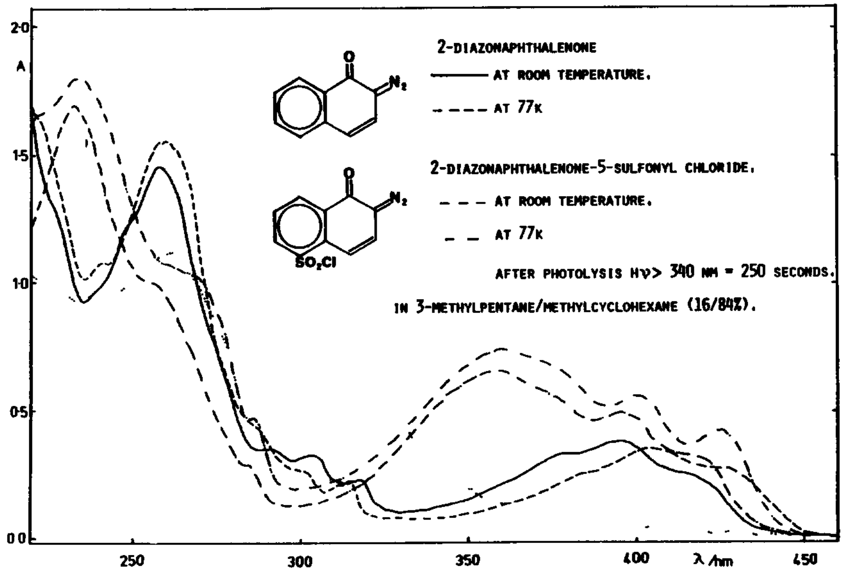


FIGURE 2. ULTRA-VIOLET SPECTRA OF 2-DIAZONAPHTHALENONE AND 2-DIAZONAPHTHALENONE-5-SULFONYL CHLORIDE.

tion at 77K (λ > 340 nm) turns the sample from yellow to colorless, and the IR spectrum showed loss of the peaks due to the starting material and new peaks at 2130 cm^{-1}, 2115 cm^{-1} (C=C=O stretch), 1450 cm^{-1}, 770 cm^{-1}, 745 cm^{-1}, and 705 cm^{-1}, plus a series of weaker peaks 1400-1800 cm^{-1}. Irradiation with unfiltered light or warming to 170K results in decomposition of these peaks. This result contrasts with those for ketene (IIIb) which is reported to be photochemically stable at 77K and thermally stable at room temperature in vacuo.[6] Irradiation (λ > 340 nm) of 1-diazonaphthalenone (I) at 77K also results in new IR peaks at 2130 cm^{-1}, 2115 cm^{-1}, 1450 cm^{-1}, 770 cm^{-1}, 745 cm^{-1}, and 705 cm^{-1} which are compatible with the ketene (IIa).

The photolysis of 2-diazonaphthalenone-5-sulfonyl chloride (IIIc) at 77K was also examined by UV and IR spectroscopy at 77K in order to assess the effect of the sulfonyl group. The UV absorption spectrum of compound IIIc showed a red shift for the bands above 300 nm upon cooling from room temperature to 77K (Figure 2) Irradiation of IIIc at 77K (λ > 340 nm) resulted in new bands at 317 nm (8.37×10^{3} M^{-1} cm^{-1}) and 264 nm (1.61×10^{4} M^{-1} cm^{-1}). IR spectra were recorded as a Nujol mull at 77K. Compound IIIc showed peaks at 2180 cm^{-1} and 2160 cm^{-1} (CN_2 stretch), 1620 cm^{-1} (C=O stretch), 1610 cm^{-1} and 1570 cm^{-1} (C=C stretch), plus a series of peaks below 1600 cm^{-1}. Irradiation (λ > 340 nm) resulted in the disappearance of the latter peaks and in the growth of a new absorption at 2140 cm^{-1} (C=C=O stretch) and new peaks below 1600 cm^{-1}. This new species is assigned the structure of the ketene (IIc). Warming to 273K resulted in only partial decomposition (∿ 50%) of the ketene. This suggests that the sulfonyl substituent stabilizes considerably the ketene intermediate relative to the parent compound IIIa.

From the results of the low temperature experiments, we conclude that photolysis of the two isomeric diazonaphthalenones (Ia and IIa) yields indenoketene (IIa), characterized by two UV absorptions at 310 nm and 250 nm, and IR peaks at 2130 cm^{-1} and 2115 cm^{-1}. This ketene is decomposed by photolysis with unfiltered light, or upon warming; whereas, ketenes with a sulfonyl substituent (IIb and IIc), are more thermally stable.

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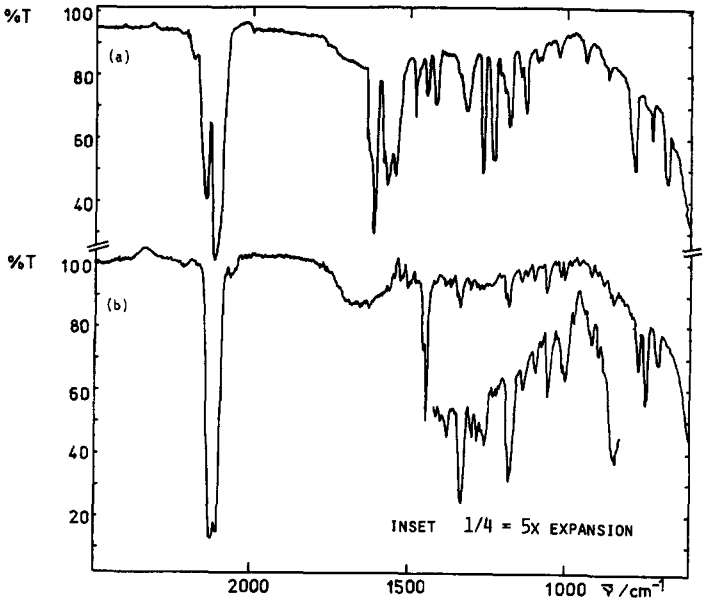
FIGURE 3. INFRA-RED SPECTRA AT 77 K. (A) 2-DIAZONAPHTHALENONE.
(B) AFTER PHOTOLYSIS $h\nu > 340$ NM = 100 SECONDS.



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