REACTIONS OF PHOTOEXCITED SO₂; PREPARATION OF α-SUBSTITUTED ALKANESULPHINIC ACIDS J.R. Nooi, P.C. van der Hoeven, W.P. Haslinghuis*

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Irradiation of SO_{2} in the <u>gas phase</u> with UV-light in the presence of gaseous alkanes leads to the formation of alkanesulphinic acids (1). When SO_{2} is irradiated in the presence of <u>cis</u>- or <u>trans</u>-butene, <u>cis/trans</u> isomerization occurs (2), whilst in the presence of blacetyl, phosphorescence from blacetyl is observed (3). Photolysis of SO_{2} within the first allowed absorption band leads to SO_{3} (4). These reactions are assumed to proceed via excited SO_{2} (2-5). The initiation of the <u>liquid-phase</u> reaction (6,7) between alkanes, SO_{2} and O_{2} (sulphoxidation, leading to alkanesulphonic acids) is also supposed to proceed via excited SO_{2} (8,9). Here we present another example of the reactivity of photoexcited SO_{2} in the <u>liquid phase</u>.

When a 2.0 molar solution of ethanol in liquid SO₂ in a pyrex NMR-tube had been irradiated with a UV-lamp (Hanau TQ-81; distance lamp to NMR-tube 0.5 cm) at -75° C for 18 h, 45% of the ethanol had reacted. According to the NMR-spectrum the ethanol was almost quantitatively converted into a compound with the structure element CH₃-CH $\langle [\delta_{CH_3} = 1.49 \text{ (d)}; \delta_{CH} = 4.49 \text{ (q)}]^{\text{str}};$ the signal of the "acid" H-atoms had increased by 53% and had shifted from $\delta = 4.1$ to $\delta = 8.4$. The product was stable up to at least -10° C (b.p. of SO₂).

Evaporation of SO₂ and neutralization with aqueous NaHCO₃ solution (temperature -10° C) permitted the isolation of a solid product, which was stable at room temperature. The NMRspectrum of the product dissolved in D₃O showed signals at $\delta = 1.28$ (d) and $\delta = 3.72$ (q) in an intensity ratio 3 : 1; the product dissolved in water was quantitatively oxidized by O₃ at room temperature into sodium 1-hydroxyethanesulphonate, CH₃CH(OH)SO₃Na [identified by IR (10) and NMR (11)].

These data are in agreement with the structure $CH_3CH(OH)SO_3Na$ for the neutralized product. This was further confirmed by the identity of its NMR-spectrum with that of sodium 1-hydroxyethanesulphinate, synthesized from ethanal and $Na_3S_3O_4$ (12). Therefore, the primary reaction

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^{**} δ-values are quoted in ppm (± 0.01) downfield from internal tetramethylsilane (measurements in liquid SO₂) or sodium 3-(trimethylsilyl)propanesulphonate (measurements in D₂O); s = singlet, d = doublet, q = quartet.

product of the photochemical reaction between SO_2 and ethanol must be the 1-hydroxyethanesulphinic acid, so far not described in literature.

When a 2.0 molar solution of 2-propanol was irradiated for 18 h as described for ethanol, 52% had reacted; 73% of the reacted 2-propanol was probably converted into 2-hydroxy-2-propane-sulphinic acid: the NMR-spectrum (-70°C) showed a singlet at $\delta = 1.47$ while the signal of the "acid" protons had increased by 49% and had shifted from $\delta = 3.4$ to $\delta = 8.7$.

When the temperature of the reaction mixture was increased to -20° C the singlet at $\delta = 1.47$ disappeared completely. The sulphinic acid was quantitatively converted into acetone* $\langle \text{ comparison} \rangle$ of GLC-retention time and NMR δ -value [$\delta_{CH_3} = 2.15$ (s) in liquid SO₂ at -20° C] with that of authentic acetone \rangle .

A number of other substrates was subjected to irradiation in liquid SO_2 under the same conditions. In Table 1, conversions and NMR-values of the products are listed. Evidently the procedure described is a facile method for producing solutions of α -substituted sulphinic acids.

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* When a mixture of a solution of 2-propanol and SO_2 (0.55 and 0.37 molar respectively) in CCl₄ was irradiated at +20°C, acetone was formed in a yield of 31 mole% in 6 h. However, also water, sulphur, chloroform and Cl⁻ ions were formed, the latter two indicating that CCl₄ is taking part in the reaction (14).

TABLE 1

Reactions of Photoexcited SO_2 at Low Temperatures Irradiation time 18 h; Temperature -75°C; Substrate Concentration 2.0 mole/1

Substrate	Product	Yield (mole %)	NMR δ-values (ppm)			
			1	2	3	4
снзон	1 Сн ₂ (SO ₂ H)он	5	4.47	_	_	· _
с ₆ н ₅ сн ₂ он	1 С ₆ Н ₅ СН(SO ₂ H)ОН	14	5.20	-	-	-
[(CH3)2CH]20 a	1 (СН ₃) ₂ С(SO ₂ H)ОСН(СН ₃) ₂	43	1.35	-	4.24	1.02
(CH ₃) ₂ CHOCH ₃ ^a	1 (СН ₃) ₂ с(so ₂ н)осн ₃	55	1.33	3.39	-	-
(сн _з сн _з) ⁵ г	1234 СН ₃ СН (SO ₂ H)SCH ₂ СН ₃	20	1.54	3.15	2.48	1.22
(Сн _э) _з сн	∫(CH ₃) ₃ CSO ₂ H	23	1.35	-	-	-
	$ \begin{bmatrix} 1 \\ CH_2 (SO_2H) & 2 \\ CH_3 (SO_2H) & CH (CH_3)_2 \end{bmatrix} $	17	1.49	~ 1.7	1.23	-
сн ³ сн ⁵ с1	CH ₃ CH(SO ₂ H)C1	5	1.99	5.27	-	-
(CH ₃) ₂ NCHO ^a	$1 CH_2 (SO_2 H) CH_3 NCHO$	35	4.37	∫3.11 ^b	8.04 ^b	-
				3.32	8.13	-

^a Irradiation time 7 h.

 $^{
m b}$ Two singlets are observed in a ratio of 1 : 1 due to rotational hindrance (13).

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