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THE PHOTOCHEMISTRY OF A STABLE SULFOXONIUM YLIDE

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It has been reported (1,2,3) that the photochemistry of sulfoxonium ylides gave interesting products which might be formed through carbene intermediates. In the continuation and extension of our studies on stable sulfoxonium ylides (4,5,6,7), we wish to report an interesting photochemical reaction of a stable sulfoxonium ylide accompanied by a complex rearrangement.

Irradiation of dimethyl sulfoxonium 1,2-dicarbomethoxy-5-carbethoxy-4-phenyl-1,4-pentadien-3-ylide (I)(6) in a mixture of EtOH-THF (1 : 2) with an ultraviolet lamp (Hanovia, 450W) for 2.5 hr. gave three products which were purified by careful chromatography on silica gel. The UV spectrum of the major product II, $C_{18}H_{18}O_6$, m.p. 106-107°[*] (37.5% yield) showed maxima at 241 mμ (log ε: 4.72), 278 mμ (3.69)(shoulder), 288 mμ (3.79), 297 mμ (3.75)(shoulder), and 334 mμ (3.15) which are characteristic of a naphthalene derivative. The NMR spectrum[**] of II exhibited signals at 2.71 ppm (3H, singlet) ascribable to a methyl group attached to an aromatic ring, 3.91 ppm (3H, singlet) and 4.01 ppm (3H, singlet) due to two kinds of methyl ester groups, 1.38 ppm (triplet, 3H, J=7.5 cps) and 4.42 ppm (2H, quartet, J=7.5 cps) assignable to an ethyl ester group, and in addition, the complex multiplet at 7.53-8.25 ppm due to aromatic hydrogens (4H). Since the starting material had no methyl group, the above UV and NMR data which showed the presence of a methylnaphthalene moiety, suggested that a complex rearrangement had occurred. The mass spectrum of this compound (II) showed a peak at m/e 330 for the molecular ion, and peaks at m/e 141 and 115 which were assignable to benzotropylium- and benzocyclopentadienyl cation, respectively, also indicating the methylnaphthalene derivative structure. In order to establish the structure of II the following chemical transformations

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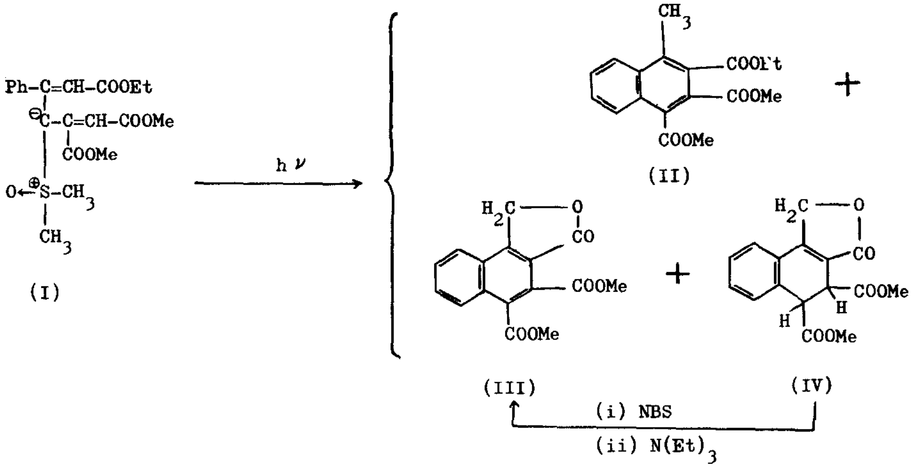
[*] All melting points are uncorrected. All new compounds cited in this paper gave satisfactory elemental analysis.

[**] NMR spectra were taken using Varian Associates A-60 and HA-100 spectrometer in deuterochloroform solution with tetramethylsilane as internal standard.



were made. Reduction of II with lithium aluminum hydride afforded a triol (V), m.p. 168-169°, which was brominated with phosphorous tribromide to give a tribromide (VI), m.p. 193-194°. Treatment of this tribromide with lithium aluminum hydride in tetrahydrofuran gave 1,2,3,4-tetramethylnaphthalene (VII) which was identical in all respects with an authentic sample prepared from 2,3-dimethylnaphthalene according to Hewett's method (8). Hydrolysis of II with sodium hydroxide solution, followed by treatment with hydrochloric acid, afforded a mixture of two kinds of carboxylic acid anhydrides. The mixture was decarboxylated, without purification, by heating in quinoline in the presence of copper powder to give 1-methylnaphthalene (VIII) which was identified by gas chromatography using three different columns. From these data and a lactonization reaction, which will be described later, the structure of II was concluded to be 1,2-dicarbomethoxy-3-carbethoxy-4-methylnaphthalene.

The second photochemical product was separated from the third by chromatography using silica gel impregnated with silver nitrate. Compound III thus obtained (0.39% yield) had a molecular formula, $C_{16}H_{12}O_6$, and melted at 180.5-182°. The UV spectrum exhibited maxima at 243 mμ (log ε: 4.79), 288 mμ (3.73), 299 mμ (3.70)(shoulder), 320 mμ (3.35)(shoulder), and 334 mμ (3.25), which are again characteristic of a naphthalene nucleus. The NMR spectrum of III gave signals at 4.00 ppm (3H, singlet) and 4.15 ppm (3H, singlet) due to two kinds of methyl ester groups, 5.60 ppm (2H, singlet) and 7.67-8.45 ppm (4H, multiplet) ascribable to aromatic hydrogens. The IR spectrum of III showed an unsaturated γ-lactone absorption at 1772 cm^{-1} (in $CHCl_3$). Therefore compound III would have a lactone moiety, structurally derived from the methyl and the carbethoxy group of II. This deduction was confirmed by the following reactions.

(II)

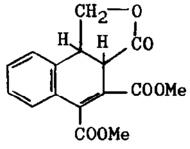
(V): R^1=H, R^2=R^3=R^4=$-CH_2OH$

(VI): R^1=H, R^2=R^3=R^4=$-CH_2Br$

(VII): R^1=H, R^2=R^3=R^4=$-CH_3$

(VIII): R^1=R^2=R^3=R^4=H

(IX): R^1=Br, R^2=-COOEt, R^3=R^4=-COOMe



(X)

Bromination of II with NBS in carbon tetrachloride afforded a monobrominated compound (IX), m.p. 109-111°, which was heated at 200° according to Hirshberg's method (9) to give the same lactone (III). Thus the structure of III was established as dimethyl 3-oxo-1,3-dihydronaphtho-[1,2-c]furan-4,5-dicarboxylate.

The third substance IV, $C_{16}H_{14}O_6$, obtained in 0.35% yield from I, melted at 165-167°. The UV spectrum of IV showed maxima at 223 mμ (plateau) (log ε: 4.21), 229 mμ (4.23) and 287 mμ (4.19), which are similar to that of trans-cinnamic acid. The NMR spectrum showed peaks at 3.64 ppm (3H, singlet) and 3.65 ppm (3H, singlet) assignable to two kinds of methyl esters, 4.28 ppm (1H, multiplet), 4.55 ppm (1H, doublet, J=2 cps), 5.08 ppm (1H, quartet, J_1=2 cps, J_2=17 cps), 5.26 ppm (1H, quartet, J_3=1 cps, J_2=17 cps) and 7.20-7.55 ppm (4H, multiplet). Double irradiation at 4.28 ppm changed the peak at 4.55 ppm into a singlet, and the signals at 5.08 and 5.26 ppm into a doublet (J=17 cps) (10), respectively. In the IR spectrum IV showed a lactone absorption at 1762 cm^{-1} (in $CHCl_3$) and in the mass spectrum a molecular ion peak at m/e 302 was observed. As in the case of II, benzotropylium- and benzocyclopentadienyl cation at m/e 141 and 115, respectively, were also recognized in the mass spectrum. These spectroscopic data suggested that IV was a dihydro derivative of III. Attempted dehydrogenation of IV with DDQ or powdered sulfur was not successful and only the starting material was recovered. Therefore, compound IV was brominated with NBS in chloroform and the resulting brominated substance, without purification, was dehydrobrominated with triethylamine to yield the second photochemical reaction product, III, whose structure had already been determined by the correlation with II. Thus, the photochemical reaction products obtained from I were intercorrelated by the chemical reactions. From these reactions only two possible structures, IV, i.e. dimethyl 3-oxo-1,3,4,5-tetrahydronaphtho[1,2-c]furan-4,5-dicarboxylate and a double bond isomer, X, remained for the third photochemical reaction product. However, structure X was definitely excluded from extensive analyses of the NMR data which will be discussed in a forthcoming paper.

The mechanism of this photochemical reaction is not clear at present, and there remains the fascinating problem of clarifying the mechanism of this deep seated rearrangement. Further investigations of this reaction are in progress.

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