August, 1987] © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***60****, 3037—3038 (1987)* 3037

Synthetic Photochemistry. XXXVIII.[1)] The Photorearrangement of the Tropone Endoperoxide, 6,7-Dioxabicyclo-[3.2.2]nona-3,8-dien-2-one

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(Received March 3, 1987)

Synopsis. The photolysis of 6,7-dioxabicyclo[3.2.2]nona-3,8-dien-2-one produced six photolysates, including a cage γ-lactone which belongs to the same type of product as was characterized in each case of the photolysis of the endoperoxides derived from 2-aryl- and 2,7-diaryltropones by Mukai et al. The new products identified were 2,7-dioxabicyclo-[3.2.2]nona-3,8-dien-6-one, a δ-lactone acetal, and 7-exo-formyl-3-oxabicyclo[4.1.0]hept-4-en-2-one, a δ-lactone.

In 1970's, Mukai et al. discovered a photorearrangement of several 1-aryl-, 3-aryl, and 1,3-diaryl-6,7-dioxabicyclo[3.2.2]nona-3,8-dien-2-ones **1a—c**, and the endoperoxides derived from 2-aryl- and 2,7-diaryltropones, to cage γ-lactones **2a—c**.[2)] Then, by means of low-temperature IR spectroscopy, they identified a bicyclic ketene as the intermediate leading to the photolysate.[3)] On this basis, they proposed a reaction sequence from the endoperoxides **1** to ketene **A** and cage lactones **2**, and explained the mechanism in terms of a transannular interaction of the enone and the isolated double bond[4)] in the molecule.

Although, unfortunately, they failed[2)] to isolate or characterize any photolysate other than **2**, it is hardly conceivable that the ketene intermediate results selectively in only one type of product. In addition, recently we ourselves have noticed a transannular interaction of the enone part and the dioxa linkage in related compounds.[5)] Furthermore, Mukai et al. have stated[2)] that no product could be identified in the photolysis mixture of the parent tropone endoperoxide, 6,7-dioxabicyclo[3.2.2]nona-3,8-dien-2-one (**3**).[6)] These findings prompted us to carry out a reinvestigation of Mukai's experiments with a synthetically useful parent compound, **3**.[7)] The results, identifying six products **4—9**, will be presented briefly.

The irradiation of a benzene solution of the parent peroxide **3** by means of a high-pressure mercury lamp caused a rapid photolysis. The products could be isolated by means of silica-gel chromatography; the structures were deduced mainly from the NMR spectra,[9)] which revealed mutually-coupled methine proton systems, allowing for a first-order analysis.

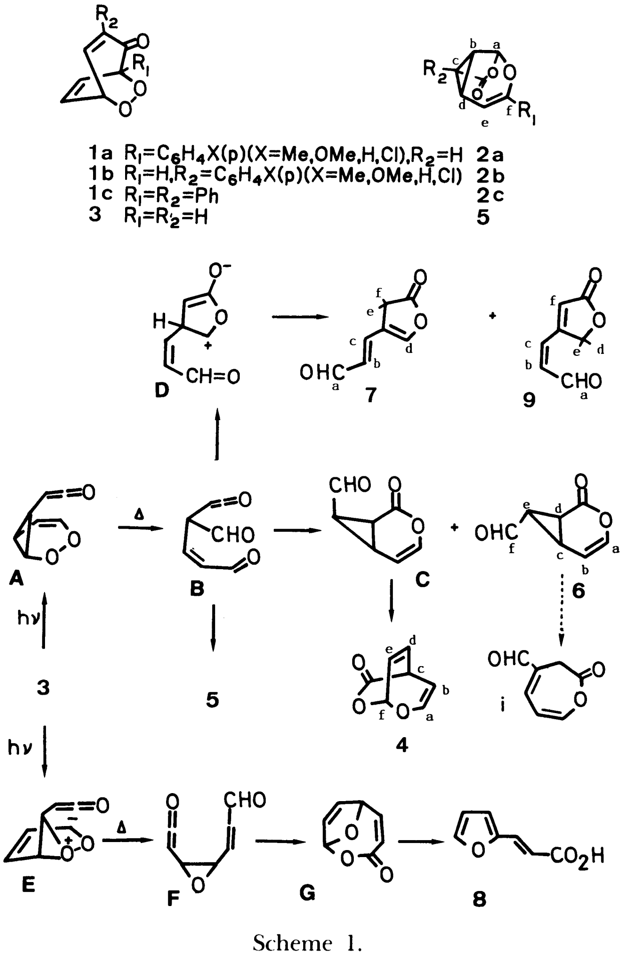
The least polar product **4**, one of the major products, was a bicyclic acetal δ-lactone, showing the carbonyl absorption[9)] at 1775 cm^{-1}; an analysis of the whole coupling sequence of protons, four of which were on the sp^2-carbons, by means of an intensive double-irradiation technique,[10)] enables us to deduce that **4** was 2,7-dioxabicyclo[3.2.2]nona-3,8-dien-6-one.

Another major product (**5**=**2**; R_1=R_2=H) was shown to be a cyclopropane-containing compound; the characteristic 4-alkoxy-γ-lactone absorption was observed at ν: 1782 cm^{-1}. The well-separated ^{1}H NMR spectrum of this tricyclic compound, 2,8-dioxatricyclo[4.2.1.$0^{5,9}$]non-3-en-7-one, showed a close resemblance to those of the reported photolysates **2a—c** from **1a—c**.[2)] The third product, an enol δ-lactone aldehyde (**6**) [IR ν: 1760 and 1715 cm^{-1}], was deduced to be 7-exo-formyl-3-oxabicyclo[4.1.0]hept-4-en-2-one on the basis of the spectroscopic data.

The fourth photolysate **7** was an aldehydic enol γ-lactone [IR ν: 1830 and 1807 cm^{-1}]; its structure was deduced by means of detailed ^{1}H and ^{13}C NMR spectral analyses.

The most polar photolysate **8** was 3-(2-furyl)acrylic acid, as was confirmed by direct comparison with an authentic sample.[11)] The remaining photoproduct **9** was obtained in a mixture with the furylacrylic acid **8**. Its ^{1}H NMR spectral data were compatible with those of 3-(2,5-dihydro-5-oxo-3-furyl)acrylaldehyde.[12)]

The present results show a much improved material balance (50% vs. trace to 21%) compared to those of previous studies by Mukai et al.[2)] It is now possible to



Scheme 1.

discuss the general features of this photorearrangement. There is no photoproduct with a peroxy group, and the absence of an alcoholic function eliminates the heterolytic cleavage of the peroxy linkage. Consequently, the peroxy group might have been transformed via the electrocyclic processes during the irradiation, but it is difficult to explain the formation of all the new photolysates by means of Mukai's mechanism, that is, via a ketene intermediate **A**. These products can thus be classified into two groups according to the *proto*-photolysates, precursor ketenes: i.e., Type I (**4**—**7** and **9**) and Type II (**8**). All the Type I products carry a branched side chain from the α- or β-carbon to the carboxylic carbon, and all could be derived from ketene **A**. Its cycloreversion should give **B**, with which an intramolecular Diels-Alder reaction should form **C** and its stereoisomer, **6**.[13] Cage lactone acetals, **4** and **5**, could be derived from **C** and **B** respectively, and the furanones, **7** and **9**, should be formed by cyclization at the ketene and aldehyde moieties of **B** to a precursor cyclisate (**D**), followed by two ways of hydrogen transfer. On the other hand, the formation of the remaining compound, **8**, a free carboxylic acid, of Type II, could be explained in terms of another precursor: The ketene **E**, with a zwitterionic peroxirane group and resulting from a transannular reaction of the α,β-unsaturated keto group and the peroxide linkage, might be isomerized to a neutral epoxy ketene (**F**), which, via a bicyclic ε-lactone (**G**), should afford **8**.

Consequently, the photolysates isolated and characterized from **3** in this study show that the reaction is not so simple as was reported by Mukai et al.; particularly, the formation of **8** must be explained by another precursor, **E**, with a peroxirane structure.

Experimental

The UV-Light Irradiation of 6,7-Dioxabicyclo[3.2.2]nona-3,8-dien-2-one. A benzene solution (5 cm^3) of **3** (163 mg) was irradiated by means of a 400-W high-pressure mercury lamp through a Pyrex glass filter at 10—20 °C under an N_2 atmosphere for 2 h. The reaction was monitored by the disappearance of the **3** in high-pressure liquid chromatography. The residual mixture obtained by the evaporation of the solvent was then chromatographed on a silica-gel column and eluted with benzene–ethyl acetate to obtain the respective products:

4 [A colorless oil, 27.3 mg; 17%. Found: C, 60.61; H, 4.64%; M. W., 138.0319. Calcd for $C_7H_6O_3$: C, 60.87; H, 4.38%; M. W., 138.0318. ^{1}H NMR δ[10]=3.29 (Hc, ddd, J=8.3, 6.4, 1.5 Hz), 5.06 (Hb, dd, J=8.3, 6.8 Hz), 5.92 (Hf, dd, J=4.4, 2.0 Hz), 5.95 (He, ddd, J=8.3, 4.4, 1.5 Hz), 6.10 (Ha, d, J=6.8 Hz), and 6.70 (Hd, ddd, J=8.3, 6.4, 2.0 Hz). ^{13}C NMR δ=39.3, 95.7, 101.7, 120.8, 136.7, 144.1, and 171.9. IR ν: 1775, 1630 cm^{-1}].

5 [A colorless oil, 30 mg; 18%. Found: C, 60.50; H, 4.37%; M. W., 138.0318. ^{1}H NMR δ=1.86 (Hd, dddt, J=8.5, 7.5, 4.5, 0.5 Hz), 2.28 (Hc, dd, J=8.5, 5.5 Hz), 2.59 (Hb, dddd, J=7.5, 5.5, 5, 0.5 Hz), 5.29 (He, dd, J=6, 4.5 Hz), 6.12 (Ha, d, J=5 Hz), and 6.35 (Hf, dd, J=6, 0.5 Hz). ^{13}C NMR δ=15.1, 15.5, 24.1, 96.3, 100.8, 141.6, and 174.0. IR ν: 1782 cm^{-1}].

6 [A colorless oil, 7.5 mg; 5%. Found: C, 60.67; H, 4.56%; M. W., 138.0302. ^{1}H NMR δ=2.27 (He, td, J=4, 2.5 Hz), 2.42 (Hc, dddd, J=8, 4.5, 4, 1 Hz), 2.78 (Hd, ddd, J=8, 4, 1 Hz), 5.55 (Hb, ddd, J=6, 4.5, 1 Hz), 6.40 (Ha, dd, J=6, 1 Hz), and 9.63 (Hf, d, J=2.5 Hz). ^{13}C NMR δ=24.8, 26.4, 34.2, 104.1, 141.7, 163.7, and 196.1. IR ν: 1760, 1715, and 1657 cm^{-1}].

7 [A colorless oil, 6.5 mg; 4%. Found: M. W., 138.0316. ^{1}H NMR δ=3.37 (He and Hf, dd, J=2, 1 Hz), 6.02 (Hb, dd, J=15.5, 7.5 Hz), 7.16 (Hc, d, J=15.5 Hz), 7.25 (Hd, t, J=2 Hz), and 9.56 (Ha, d, J=7.5 Hz). ^{13}C NMR δ=31.5, 128.5, 129.7, 141.0, 147.7, 173.1, and 192.7. IR ν: 1830, 1807, 1680, and 1630 cm^{-1}].

8 [Colorless crystals, mp 132—133 °C (lit,[11] mp 138 °C), 6.3 mg; 4%. ^{1}H NMR δ=6.28 (1H, d, J=15.5 Hz), 6.45 (1H, dd, J=3.5, 2 Hz), 6.63 (1H, d, J=3.5 Hz), 7.47 (1H, d, J=15.5 Hz), and 7.47 (1H, dm, J=2 Hz). δ(DMSO)=6.13 (1H, d, J=15.5 Hz), 6.60 (1H, dd, J=3.4, 1.7 Hz), 6.90 (1H, d, J=3.4 Hz), 7.36 (1H, d, J=15.5 Hz), and 7.80 (1H, d, J=1.7 Hz)].

9 [A colorless oil, 3.2 mg; 2%. ^{1}H NMR δ=5.02 (Hd and He, dd, J=2, 1 Hz), 6.29 (Hb, t, J=7 Hz), 6.40 (Hf, br s), 6.42 (Hc, d, J=7 Hz), and 9.70 (Ha, d, J=7 Hz)].

We wish to thank Professor Mitsuaki Kodama, of Tokushima Bunri University, for providing us with a valuable 400 MHz NMR spectrum of **4**. We are also grateful to the Ministry of Education, Science, and Culture for its financial support, the Grant-in-Aid for Scientific Research given to A. M. (No. 60470025).

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8) The NMR spectra were measured in $CDCl_3$ solutions, unless otherwise stated, and the chemical shifts were expressed in δ units. The IR spectra were taken as liquid films.

9) The $\nu_{(C=O)}$ of 1,5,5-trimethyl-2,6-dioxabicyclo[2.2.2]-octan-3-one appeared at 1773 cm^{-1}. See I. D. Rae and A. M. Redwood, *Austr. J. Chem.*, **27**, 1143 (1974).

10) This was analyzed by means of the 400-MHz ^{1}H NMR spectrum.

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12) The carboxylic acid function could not be derived by an auto-oxidation of the aldehydic function; **4**—**7**, and **9** are all on the same oxidation level as **8**.

13) Frequently, an aldehyde **i**, apparently derived from **6**, was identified among the photolysates; its ^{1}H NMR spectrum [δ=3.16 (2H, s), 6.38 (1H, dd, J=12, 6 Hz), 6.98 (1H, d, J=6 Hz), 6.98 (1H, d, J=12 Hz), and 9.48 (1H, s)] indicated the structure depicted.