Photoinduced Transannular Reaction of 4,5-Octamethylene-1,3-dioxolen-2-one

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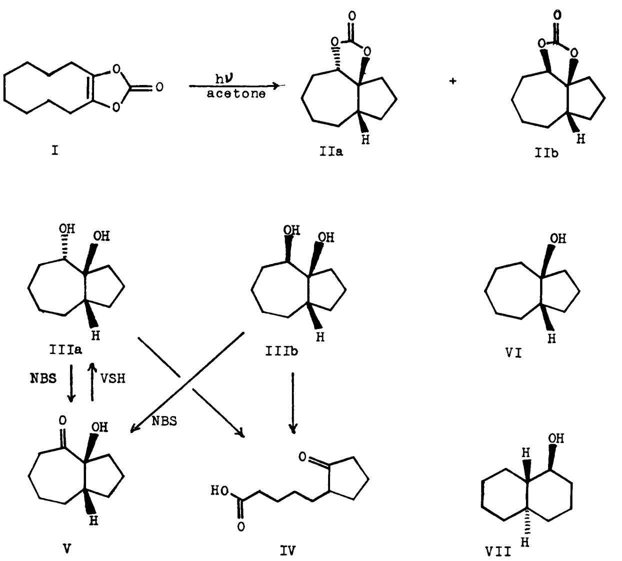
Recently, 1,3-dioxolen-2-one (vinylene carbonate) has been reported to undergo dimerization[1] or cycloaddition[2] on UV irradiation. However, the photoreaction of compound I[3,4] given in the title proceeded in quite a different way as described below.

A 0.2M solution of I in acetone was irradiated under N_2 with a 200 W high-pressure Hg lamp. The photolysate was distilled to give a mixture of stereoisomers[4] (IIa and IIb, 71% yield) which were isomeric with I as established by means of MS (M^+ *m/e* 196) and elemental analysis. The mixture exhibited an IR band at 1795 cm^{-1} characteristic of a 1,3-dioxolan-2-one system. The NMR signal of the methine proton adjacent to oxygen appeared at δ 4.65—4.75. As separation of IIa and IIb was unsuccessful, the mixture was converted into the corresponding *vicinal* diols (IIIa: IIIb= 5.7: 1). The structure and stereochemistry of IIIa[4] (mp 82—83°C, M^+ *m/e* 170, IR 3400 cm^{-1}) and IIIb[4] (M^+ *m/e* 170, IR 3480 cm^{-1}) were determined as follows. (1) Since the glycol cleavage of IIIa and IIIb with $NaIO_4$ and $KMnO_4$ yielded the same keto acid IV (1735, 1710 cm^{-1}, oxime mp 121—124°C (lit,[5] 124—125.5°C), semicarbazone mp 192—193°C (lit,[5] 195—196°C)), both IIIa and IIIb should have a bicyclo-[5.3.0]decane structure. (2) As the oxidation of IIIa and IIIb with *N*-bromosuccimide (NBS)[6] afforded the same ketol V[4] (IR 3460, 1700 cm^{-1}), they shoud have the same mode of ring fusion. (3) The reduction of V with $NaH_2Al(OCH_2CH_2OMe)_2$ (VSH) gave IIIa exclusively: the *trans*-configuration of the *vicinal* hydroxyl groups of IIIa was established on the basis of Cram's rule. (4) The half tosylation of the mixture of IIIa and IIIb followed by reduction with $LiAlH_4$ in ether or $NaBH_4$ in dimethyl sulfoxide, afforded *cis*-bicyclo[5.3.0]decan-1-ol (VI)[7] along with *trans, trans*-α-decalol (VII).[8] In conclusion, IIIa and IIIb were characterized as *cis*-bicyclo[5.3.0]decane-*trans*-1, 2-diol and its *cis*-diol isomer, respectively.



The transannular reaction of I proceeded as well upon benzene-sensitization. Intramolecular hydrogen-abstraction by the excited olefinic bond in its triplet state and the subsequent recombination of the resulting diradical may account for the new photoreaction.[9] In contrast to the mother compound, the derivative I underwent no cycloaddition to ethylene or acetylene on attempted acetone-sensitized reaction. The intramolecular reaction predominated even in 2-propanol containing benzene sensitizer.

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1) W. Hartmann and R. Steinmetz, *Chem. Ber.*, **100**, 217 (1967).

2) a) W. Hartmann, *ibid.*, **101**, 1643 (1968). b) H.-D. Scharf, W. Droste, and R. Liebig, *Angew. Chem.*, **80**, 194 (1968).

3) Compound I (mp 44—45°C, IR 1822, 1731 cm^{-1}, NMR: no olefinic protons) was prepared by the reaction of sebacoin with phosgene in the presence of pyridine or by ethoxycarbonylation of sebacoin and subsequent acid treatment.

4) All the new compounds gave correct data on elemental analyses.

5) W. Herz, *J. Org. Chem.*, **22**, 630 (1957).

6) L. F. Fieser and S. Rajagopalan, *J. Amer. Chem. Soc.*, **71**, 3938 (1949).

7) An authentic sample of VI was prepared by the hydroboration of $\Delta^{1(7)}$-bicyclo[5.3.0]decene.

8) Formation of VII may be ascribed to the base-catalyzed rearrangement of tosylates. Similar rearrangements have been reported, *e.g. cf.* G. Büchi, W. Hofheinz, and J. V. Pauksteils, *J. Amer. Chem. Soc.*, **91**, 6473 (1969).

9) Photoinduced transannular reaction has been reported only in a sterically compressed system of a methylene and an olefinic bond. *Cf.* H.-D. Scharf, *Tetrahedron*, **23**, 3057 (1967); L. Vollner, H. Parler, W. Klein, and F. Korte, *ibid.*, **27**, 501 (1971).