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PHOTO-SMILES REARRANGEMENTS

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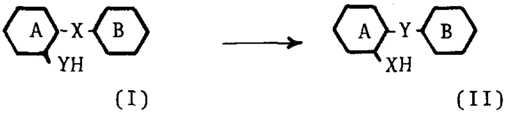
Rearrangements involving intramolecular nucleophilic substitutions as shown in eq. 1 are well known as Smiles rearrangement.

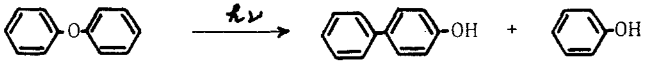


(1)

where X : O, S, CO_2 and SO_2.
YH : OH, NH_2, $CONH_2$, NHAcyl and SH.
A : Substituted phenyl or other aromatic group.
B : Substituted phenyl or nitrogen heteroaromatic group.

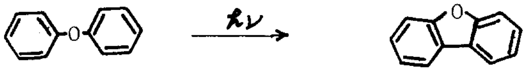
The Smiles rearrangements in the ground state of such organic molecules as I have been extensively studied.[1-5] For example, 2',4'-dinitro-2-aminodiphenyl ether rearranges to give 2',4'-dinitro-2-hydroxydiphenylamine in aqueous and alcoholic solutions.[2,4] Recently, it has been also shown that the Smiles rearrangements of pyridine[3] and s-triazine[5] derivatives take place in the presence of acid.

While, the photochemical reaction of diphenyl ether gives p-phenyl phenol and phenol in alcoholic solutions as shown in eq. 2.[6]



(2)

Stegemeyer[7] has reported that the photocyclization of diphenyl ether occurs in addition to ep. 2.



(3)

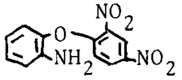
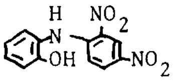
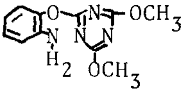
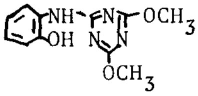
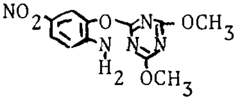
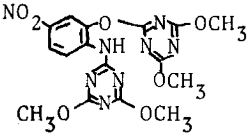
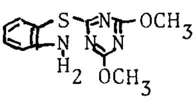
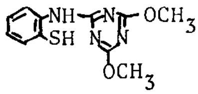
However, in the case of diphenyl thioether no photocyclization has been observed.

Therefore, it is of interest what kind of photochemical reactions would occur in the molecules like I. In the present work, the photochemical reactions of the aromatic molecules having such molecular structure as I described in eq. 1 have been carried out. A low pressure mercury lamp were used as the 2537 Å radiation source with a Vycor glass filter. A high pressure mercury lamp was also used as the radiation source of longer wavelengths than ~3000 Å with a Pyrex glass filter. The starting materials containing s-triazine group were synthesized by treating 2-chloro-4,6-dimethoxy-s-triazine with o-aminophenol, 5-nitro-2-aminophenol and o-aminothiophenol respectively.

The irradiated solutions were condensed, then the products were separated and purified by column chromatography. The identifications of these products were performed by means of nmr, infrared, mp, elemental analyses, and the solubility in an alkaline solution in comparion with those of authentic samples. It was found that the photochemical reactions of some aromatic molecules of type I gave the corresponding Smiles rearrangement products accompanied with some side-reaction products. It was also comfirmed that no rearranged product was obtained without UV-light in the solvents used and at room temperature.

These preliminary results are shown in Table 1.

Table 1. The Photo-Smiles Rearrangements of
Some Aromatic Compounds at Room Temperature.

Substance	Solvent	Radiation source	Irradiation time hr.	Photo-Smiles rearrangement product
	Benzene	H(>3000Å)	24	
	Benzene	H(>3000Å)	50	
	Ethanol	L(2537A) and H(>3000A)	50 24	No
	Ethanol	L(2537Å)	40	No
	Ethanol	L(2537Å) and H(>3000Å)	30 24	

H: High pressure mercury lamp. L: Low pressure mercury lamp.

A mechanistic study concerning the photo-Smiles rearrangement is in progress, and it will be reported in the near future.

References

(1) E.g., L.A.Warren and S.Smiles, J.Chem.Soc., 1931, 914.

(2) K.C.Roberts and C.G.de Worms, ibid, 1934, 727,
K.C.Roberts, C.G.de Worms and H.B.Clark, ibid, 1935, 196.

(3) O.R.Rodig, R.E.Collier, and R.K.Schlatzer, J.Org.Chem., 29, 2652(1964)

(4) F.W.Balfour and T.F.Fagley, J.Phys.Chem., 72, 1300(1968).

(5) I.Harayama, S.Sekiguchi, and K.Matsui, Submitted for publication in J.Heterocyclic Chem.

(6) M.S.Klarasch, G.Stampa, and W.Nudenberg, Science, 116, 309(1952).

(7) H.Stegemeyer, Naturwissenschaften, 53, 582(1966).