CHEMISTRY LETTERS, pp. 943-946, 1980.

PHOTOLYTIC α-ELIMINATION OF ORGANIC HALIDES FROM ORGANOTELLURIUM(IV) HALIDES

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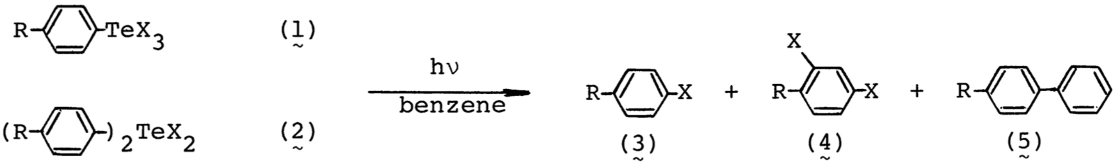
Irradiation of organotellurium(IV) halides in benzene affords the corresponding organic halide by α-elimination, the carbon-halogen bond being formed at ipso-position and in some case retentively. The reaction is not affected by the presence or absence of oxygen and t-butoxy radical.

In the numerous works on organotellurium compounds,[1)] the photolytic carbon-tellurium bond fission has been the subject of recent interest and yet been limited only to organotellurium(II) compounds.[2)] We now report a first example of the photochemical reaction of easily accessible organotellurium(IV) halides where a new type photolytic α-elimination occurred to give the corresponding organic halides.

Photolysis of p-anisyltellurium(IV) trichloride (1; R=MeO, X=Cl)(1 mmol) in benzene(200 cm^3) with a high pressure mercury lamp at 20-30°C for 1 h in the presence of atmospheric oxygen afforded p-chloroanisole (3; R=MeO, X=Cl) in 70% yield (0.70 mmol) together with a small amount of 2,4-dichloroanisole (4; R=MeO, X=Cl) (2%, 0.02 mmol), and 4-methoxybiphenyl (5; R=MeO)(1%, 0.01 mmol), none of o-chloroanisole being formed. The reaction was accompanied by the deposition of black metallic tellurium(0.31 mmol) which may be formed by disproportionation of the preformed $TeCl_2$. Elongation of the reaction time to 4 h increased the yield of (3)-(5), but decreased the selectivity for (3). The photo-oxidation of benzyltellurium(II) compounds has been known to give the oxygen-containing compounds such as benzaldehyde and benzyl alcohol.[2a)] No methoxyphenols, however, were



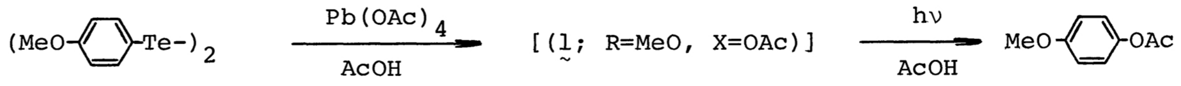
formed in our reaction even when the reaction was carried out under oxygen atmosphere. In fact, this photolysis was not affected by the presence or absence of oxygen. In the cases of diaryltellurium(IV) dichlorides (2; X=Cl) the yields of the products were generally lower than those from (1; X=Cl). Here, no precipitation of a tellurium metal occurred and instead a mixture of inorganic and organic tellurium salts was precipitated.3) The amount of the coupling products with solvent benzene, (5; X=MeO or Me), increased in these cases. Any trace of a symmetrical biaryl was not produced in all cases. Typical results are shown in the table. Various organic solvents such as acetic acid, acetonitrile, 1,4-dioxane, chloroform, and toluene could be used in the place of benzene.

Table. Photolysis of (1) and (2) at 20-30°C in benzene

(1) or (2) (1 mmol)	Irradiation time[a] (h)	Yield/%[b] (3)	(4)	(5)
(1; R=MeO, X=Cl)	1	70	2	1
(1; R=MeO, X=Cl)	1[c]	68	2	1
(1; R=MeO, X=Cl)	1[d]	76	2	trace
(1; R=MeO, X=Cl)	1[e]	72	2	trace
(1; R=MeO, X=Cl)	4	81	10	4
(1; R=Me, X=Cl)	4	36	2	trace
(2; R=MeO, X=Cl)	4	37	1	6
(2; R=MeO, X=Cl)	4	17	1	13
(1; R=MeO, X=Br)	4	30	0	trace

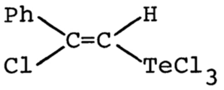
[a] In the presence of atmospheric oxygen; benzene 200 cm^3. [b] Determined by GLC; 1 mmol and 2 mmol of (3)-(5) correspond to 100% yield in the case of (1) and (2), respectively. [c] Under N_2. [d] Under O_2. [e] $(t\text{-BuO})_2$ 0.5 mmol added.

Photolysis (4 h) of p-anisyltellurium(IV) tribromide (1; R=MeO, X=Br) in benzene and of di(p-anisyl)tellurium(IV) diacetate (2; R=MeO, X=OAc) in acetic acid gave the corresponding (3) selectively in 30% and 6% yield, respectively. Similar treatment of acetic acid solution of (1; R=MeO, X=OAc), prepared in situ from di(p-anisyl)ditelluride and lead(IV) acetate, produced (3; R=MeO, X=OAc) in 14% yield.



The facts that the chlorine and the bromine were introduced selectively to the position where tellurium moiety was attached previously and that solvent benzene was scarcely incorporated represent a characteristic feature of aryltellurium(IV) trihalide, since UV irradiation in several arylmetal chlorides (metal=Hg, Tl, or Si) in benzene scarcely afforded aryl chloride and gave arylated benzene only in the case of thallium.[4)]

When (6) prepared from phenylacetylene and $TeCl_4$[5)] was irradiated in benzene at 20-25°C for 15 min, (7) was produced in 39% yield, the reaction being accompanied by the deposition of a black tellurium metal. Similarly, photolysis of (8) prepared from cyclohexene and $TeCl_4$[6)] gave (9) in 28% yield, the tellurium precipitation being scarcely observed in this case. Elongation of the reaction time resulted in the formation of various unidentified compounds by sacrificing (7) and (9). The formation of (7), Z-isomer, from (6) shows that the α-elimination occurred with retention of configuration. On the other hand, the stereochemical course of the formation of (9) from (8) is not known, since the stereochemistry of (8) has not yet been elucidated.[6)]



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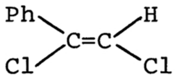
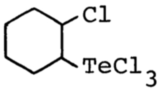


(7)



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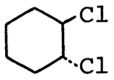

(9)

Although the mechanism of this reaction is not yet clear, a selective formation of carbon-halogen bond at ipso-position, a retentive elimination and a very limited incorporation of solvent benzene suggest that the photolysis of organotellurium(IV) trihalides does not involve a free carbon radical species in the main reaction course even if a radical fission of the C-Te bond and/or Te-Cl bond occurred. Moreover, we have confirmed separately that the addition of di-t-butyl peroxide in the reaction system of (1; R=MeO, X=Cl), (2; R=Me or MeO, X=Cl), and (8) did not give a large effect on the yield and ratio of product. This fact may exclude the possibility of the presence of such an intermediate as $R\dot{T}eX_3Z$ (Z=OR or halogen etc.) in this photolysis. The photo-induced intramolecular 1,2-metal halogen shift may operate just like as 1,2-metal oxygen shift which has been postulated in the oxidative cleavage of alkyl phenyl telluride.[7)] Further mechanistic studies and application to other organotellurium(IV) compounds are now in progress.

We thank Prof. Masaya Okano and Dr. Takashi Kawamura for their helpful discussion and Mr. Mikio Wakasugi for some experiments. The Grant in Aid for Scientific Research from the Ministry of Education, Japan is also acknowledged.

References

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3) For example, in the experiments using 0.413g(1 mmol) of (**2**; R=MeO, X=Cl) 0.14g of grey precipitates were obtained. IR spectrum of those showed the presence of p-anisyl group, but a combustion analysis showed very low C and H contents; C, 8.71%, H, 1.09%.

4) Photolysis of a heterogeneous solution of p-anisylthallium dichloride in benzene for 4 h afforded 4-methoxybiphenyl in 5% yield and none of p-chloroanisole. It has been known that photolysis of arylthallium ditrifluoroacetates in benzene gave a good yield of unsymmetrical biphenyls: E. C. Taylor, F. Kienzle, and A. McKillop, J. Am. Chem. Soc., 92, 6088(1970).

5) S. Uemura, H. Miyoshi, and M. Okano, Chem. Lett., 1979, 1357.

6) M. de Moura Campos and N. Petragnani, Tetrahedron Lett., 1959, 11. Consideration of the recent report on the stereochemistry(trans) of $TeCl_4$-1,5-cyclooctadiene addition product[7] may lead (**8**) to be trans as has been proposed by these authors. If so, the conversion of (**8**) to (**9**) is also retentive.

7) J. Bergman and L. Engman, J. Organometal. Chem., 181, 335(1979) and references therein.

(Received June 3, 1980)