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TELLURIUM DIOXIDE OXIDATION OF STILBENE DIBROMIDES TO BENZILS

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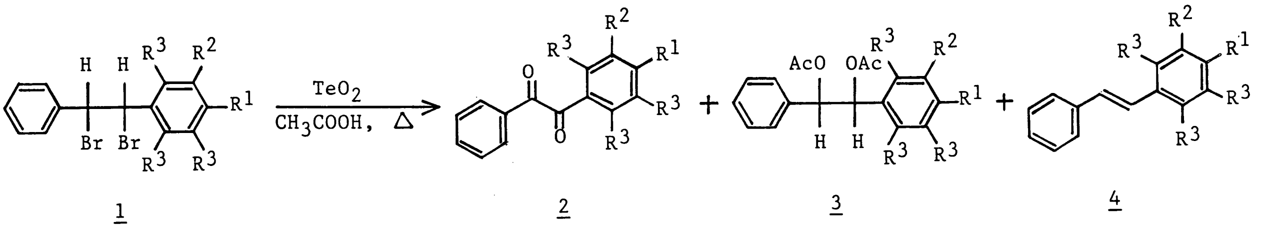
Tellurium dioxide reacts with stilbene dibromides in hot acetic acid to give benzils in good to moderate yields.

Although selenium dioxide is widely used as a laboratory oxidizing agent, the use of tellurium dioxide (TeO_2) for such purposes is so far limited in scope. Sporadic reports only describe the uses of TeO_2 in combination with acetic acid and lithium bromide for acetoxylation of olefins[1] and ketones;[2] acetoxymethylation of arenes,[2,3] and acetolysis of benzyl bromides.[2] In the present paper we wish to disclose an interesting mode of oxidizing ability of this reagent, which to the best of our knowledge has not been reported before and may find some utility in organic synthesis.

When stilbene dibromide (1) is heated with TeO_2 in acetic acid under gentle reflux, smooth oxidation occurs at benzylic positions to give benzil (2) as the major product. No C-C bond cleavage leading to the formation of benzaldehyde or benzoic acid is observed.



The reaction is apparently subject to polar effect; strongly electron-withdrawing groups on the aromatic ring favor acetolysis to diacetate (3) over oxidation to diketone 2. Thus, the substrates bearing the nitro or cyano group afford 3 as the major product under similar conditions. With these compounds, (E)-stilbene (4) is obtained as a side product (Table 1). The reaction is also subject to steric effect; hindered dibromide 1f tends to form stilbene 4f rather than benzil 2f.

The present oxidation procedure works quite well with moderately activated 1. On a similar treatment, however, *vic*-dibromoalkanes simply undergo acetolysis to furnish *vic*-diacetates, while 1,2-dibromo-1-phenylpropane gives 2-bromo-1-phenylpropyl acetate in 85% isolated yield. Diacetate 3 remains unaffected toward further action of TeO_2.

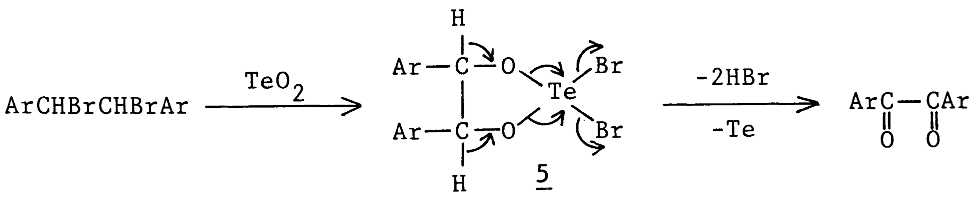
Table 1. Oxidation of stilbene dibromides with tellurium dioxide[a)]

	Dibromide 1			Reaction	Mp	Benzil 2	Diacetate 3	Stilbene 4
	R^1	R^2	R^3	time/h	$\theta_m/^{\circ}C$	Yield/%	Yield/%	Yield/%
a	H	H	H (*meso*)	3	95-96	60	—	4
b	H	H	H (*d,l*)	3	95-96	59	—	4
c	MeO	H	H	0.3	oil	60	—	14
d	$-OCH_2O-$		H	1	84-88	72	—	—
e	Me	H	H	3	oil	82	—	17
f	Me	Me	Me	3	119-127[b)]	21	—	28
g	Cl	H	H	3	75-76	86	—	15
h	NO_2	H	H	3	140-142	19	37	20
i	CN	H	H	3	—	trace	60	30

a) Stilbenes prepared by the Wadsworth-Emmons procedure were converted to dibromides using pyridinium hydrobromide perbromide. Products were identified by mass, IR, and ^1H NMR spectra as well as by direct comparison with authentic samples. Yields are based on the isolated compounds.

b) Sinters upon heating.

The mechanism of the TeO_2 oxidation is not clear at present. A possible mode of reaction may be depicted as follows: The tellurium-oxygen moiety inserts into the activated C-Br bonds of 1 to form a cyclic intermediate (5), which collapses in a way as indicated to afford benzil 2.



The general procedure is as follows: A mixture of stilbene dibromide (1, 1.0 mmol), TeO_2 (1.2-1.5 mmol), and glacial acetic acid (5 ml) was heated under gentle reflux. As the reaction proceeded, metallic tellurium began to deposit. After 1 to 3 h, water (10 ml) and chloroform (20 ml) were added to the reaction mixture and tellurium deposit was removed by filtration through a thin layer of Celite. The organic phase was separated, washed with 5% aqueous sodium hydrogencarbonate and water, dried over sodium sulfate, and then evaporated. The residue was chromatographed on silica gel using hexane-ether (10:1) as eluent. Stilbene eluted first, followed by benzil and diacetate.

References

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2) J. Bergman and L. Engman, J. Org. Chem., 47, 5191 (1982).
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