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TITANIUM-MEDIATED REDUCTION OF NITROBENZENES AND BENZIL WITH DIALKYL TELLURIDE

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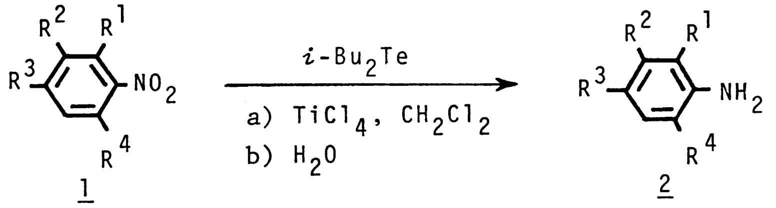
In the presence of titanium(IV) chloride, nitrobenzenes are easily reduced with dialkyl telluride to give the corresponding amines in good to moderate yields. Benzil is reduced to benzoin which, on a further treatment, is converted to desoxybenzoin.

Although organic tellurides combine with halogens or alkyl halides to produce tellurium(IV) compounds, their ability as a reducing agent does not seem to have been mentioned before. In combination with appropriate mediator, however, organic tellurides can behave as an effective reducing agent for certain oxygen-containing functionalities. Herein we disclose two types of such reduction with dialkyl telluride where aromatic nitro and 1,2-dicarbonyl compounds are involved as substrate.

Thus, when titanium(IV) chloride was added to a solution of aromatic nitro compound (1) and diisobutyl telluride in dry dichloromethane at room temperature, a purple color developed and soon turned brown.$^{1)}$ Aqueous treatment of the reaction mixture followed by usual work-up afforded the corresponding aniline (2) (Table 1). No reaction took place in the absence of titanium(IV) chloride.



Better results were obtained when nitro compound 1 was added to a deep blue solution freshly prepared by adding titanium(IV) chloride to a solution of dialkyl telluride in dichloromethane, which is a solvent of choice although other inert solvents such as benzene, chloroform and carbon tetrachloride may also be used. Aromatic tellurides are less effective in reducing nitro compounds and the products are usually accompanied by azo compounds. They are also complicating with respect to product isolation.

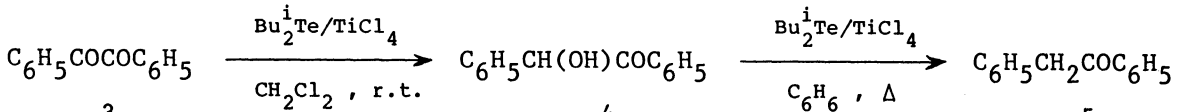
On a similar treatment, benzil (3) was reduced with moderate ease to benzoin

Table 1. Aromatic amines 2 obtained by reduction of nitro compounds 1

Nitro compound 1				Aromatic amine 2
R^1	R^2	R^3	R^4	Yield/%[a)]
H	H	H	H	74
H	CN	H	H	42
H	H	Cl	H	59
H	H	Br	H	74
H	H	C_6H_5	H	92
H	H	C_6H_5CO	H	72
CH_3	H	CH_3	CH_3	98

a) Yields refer to isolated compounds and are not optimized.

(4), which in turn was converted slowly to desoxybenzoin (5). However, ordinary ketones remained unaffected.



$$\underset{\textbf{3}}{C_6H_5COCOC_6H_5} \xrightarrow[CH_2Cl_2\text{ , r.t.}]{Bu^i_2Te/TiCl_4} \underset{\textbf{4}}{C_6H_5CH(OH)COC_6H_5} \xrightarrow[C_6H_6\text{ , }\Delta]{Bu^i_2Te/TiCl_4} \underset{\textbf{5}}{C_6H_5CH_2COC_6H_5}$$

Although the mechanism of the reduction by dialkyl telluride is not clear at present, a likely explanation is that titanium(IV) chloride is first reduced to some low-valent titanium species, which then reacts with aromatic substrate 1 or 3 to afford the respective reduction products 2[3)] and 4.[4)]

The general procedure for reducing nitrobenzenes is as follows: To a mixture of diisobutyl telluride (1.5 mmol) and 1 mol dm^{-3} solution of titanium(IV) chloride in dichloromethane (4 ml), aromatic nitro compound (1; 0.5 mmol) in the same solvent (2 ml) was added at room temperature under nitrogen. An instantaneous reaction occurred and the color of the solution turned dark brown. The mixture was stirred for further 0.5 h and then sodium chloride (3-4 g) followed by 1 mol dm^{-3} aqueous sodium hydroxide was added until aqueous phase became alkaline. The organic phase was extracted with ether and the extract was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified by chromatography on silica gel using a 5:1 mixture of dichloromethane and ether as an eluant to obtain amine 2 in satisfactory state of purity.

References

1) An observation that the addition of aldehyde to the reaction mixture thus obtained immediately led to N-arylaldimine is of mechanistic interest, since it may suggest tellurilimine as a possible precursor of aniline.[2)]
2) H. Suzuki, S. Takeda, and Y. Hanazaki, Chem. Lett., 1985, 679.
3) T.-L. Ho and C.M. Wong, Synthesis, 1974, 45.
4) T.-L. Ho and G.A. Olah, Synthesis, 1976, 815.

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