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REDUCTION OF AROMATIC NITRO COMPOUNDS TO AMINES BY BENZENETELLUROL1)

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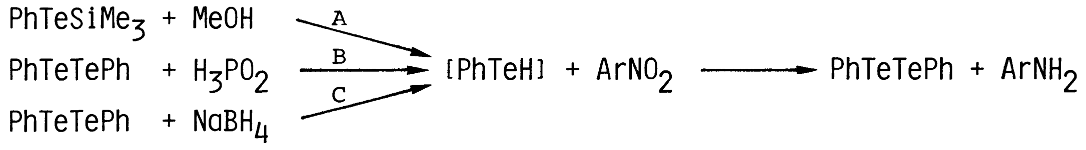
Benzenetellurol was conveniently generated by methanolysis of phenyl trimethylsilyl telluride or reduction of diphenyl ditelluride with phosphinic acid or sodium borohydride, and smoothly reduced aromatic nitro compounds to the corresponding amines.

Hydrogen telluride (H_2Te)2) and sodium hydrogen telluride (NaTeH)3,4) have recently been recognized as new effective reducing agents. A similar high reactivity due to such H-Te bond dissociation may be predicted for organotellurols. Actually organotellurols have not been isolated yet because of their ready autoxidation to ditellurides. In this regard we have examined the reducing capacity of benzenetellurol. Oae et al. reported that analogous benzeneselenol could reduce nitrobenzene to aniline at 100 °C in one day.5) On the other hand, the preceding two reagents H_2Te and NaTeH reacted with nitrobenzene at room temperature to give discrepant products of aniline2) and azoxybenzene,4) respectively. We now report the in situ generation of benzenetellurol and its successful reduction of aromatic nitro compounds to amines.

Benzenetellurol was generated in situ by the following three method: A) methanolysis of phenyl trimethylsilyl telluride; B) reduction of diphenyl ditelluride with phosphinic acid; C) reduction of diphenyl ditelluride with sodium borohydride. When methanol was slowly added into a stirred solution of



1-nitronaphthalene and phenyl trimethylsilyl telluride6) (1.2 equiv.) in carbon tetrachloride at room temperature under argon, 1-naphthylamine was obtained in 79% isolated yield, together with almost quantitative yield of diphenyl ditelluride. On the other hand, one might expect that reduction by method B and C proceeds with a redox circulation of diphenyl ditelluride. Thus, treatment of 1-nitronaphthalene with diphenyl ditelluride (0.06 equiv.) and phosphinic acid (1.6 equiv.) in aqueous tetrahydrofuran under reflux for half a day gave rise to 1-naphthylamine in a very low yield (11%). In this case, other side reactions with phosphinic acid presumably preceded the reduction. An alternative

Table 1. Reduction of aromatic nitro compounds to amines by benzenetellurol, generated in situ from diphenyl ditelluride and sodium borohydride[a)]

Run	Nitro compound	Temp/°C	Product	Yield/%
1	Nitrobenzene	80	Aniline	72
2	Nitrobenzene	55	Aniline Azoxybenzene	32 39
3	*o*-Nitrotoluene	80	*o*-Toluidine	77
4	*m*-Nitrotoluene	80	*m*-Toluidine	82
5	*p*-Nitrotoluene	80	*p*-Toluidine	83
6	2,4-Dimethylnitrobenzene	80	2,4-Dimethylaniline	86
7	*o*-Nitroanisole	80	*o*-Anisidine	95
8	*p*-Nitroanisole	80	*p*-Anisidine	89
9	*o*-Chloronitrobenzene	80	*o*-Chloroaniline	95
10	*o*-Bromonitrobenzene	80	*o*-Bromoaniline	93
11	*o*-Iodonitrobenzene	80	*o*-Iodoaniline	85
12	*m*-Dinitrobenzene	80	*m*-Phenylenediamine	65
13	*o*-Nitrobenzonitrile	80	Anthranilamide[b)]	87
14	1-Nitronaphthalene	55	1-Naphthylamine	99
15	1-Nitronaphthalene	RT	1-Naphthylamine Azoxynaphthalene	38 37
16	1,5-Dinitronaphthalene	55	1,5-Diaminonaphthalene	92

a) Reaction time, 15 h; Solvent, 3:2:1 v/v benzene-ethanol-water.
b) Accompanied with hydrolysis of cyano group.

reduction using sodium borohydride (Method C) in a mixed solvent of benzene-ethanol-water at room temperature gave a mixture of 1-naphthylamine (38%) and azoxynaphthalene (37%). Azoxynaphthalene was no longer converted to 1-naphthylamine even after prolonged treatment. However, reaction at 55 °C led to a satisfactory improvement in the yield (99%) of 1-naphthylamine. The complete circulation of diphenyl ditelluride seems to require such a higher temperature. Various nitrobenzenes were reduced to the corresponding anilines in high yields at 80 °C. The results are summarized in Table 1.

It may be thus concluded that benzenetellurol has a powerful reducing ability and supplements classical methods for the reduction of aromatic nitro compounds like hydrogen tellurides.

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