1382 © *1989 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, **62**, *1382—1384 (1989)* [Vol. 62, No. 4

Reduction of Halonitrobenzenes with Disodium Ditelluride in *N,N*-Dimethylformamide

Ralph A. ZINGARO* and Chris HERRERA
Department of Chemistry, Texas A & M University, College Station, Texas 77843, U.S.A.

(Received June 6, 1988)

Synopsis. The reaction of disodium ditelluride in *N,N*-dimethylformamide with *o*-halonitrobenzenes results in displacement of the halide, reduction of the nitro group and a ring closure reaction which yields phenazines.

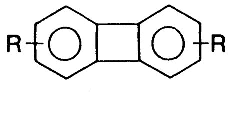
Recently, we reported on the unusual stabilities of bis(benzenetellurenyl) selenides when a carbonyl group is located ortho to the tellurium atom.1,2) This stability was attributed to a strong Te⋯O=C interaction as reflected in a relatively short Te⋯O distance (2.658 Å). As an extension of this observation it was decided to synthesize bis(*o*-nitrophenyl) ditelluride and determine its crystal structure. It would be of interest to determine the geometry of the Te-O-C-C-N-O sequence and the Te⋯O bond length in order to learn whether the Te⋯O interaction represents a more general phenomenon. Because bis(*o*-nitrophenyl) diselenide has been prepared by the reaction between *o*-chloronitrobenzene and sodium diselenide,3a) the synthesis of the ditelluride by the aromatic nucleophilic displacement reaction of sodium ditelluride on *o*-chloronitrobenzene in *N,N*-dimethylformamide was attempted. However, the only products isolated were phenazine and, in very low yield, bis(dimethylcarbamoyl) ditelluride. The latter compound was first obtained by Suzuki and Inouye3b) and its crystal structure was determined by us.4) In this same study, the latter investigators reported that aromatic nitro compounds are reduced to azo compounds by sodium telluride in DMF. These workers investigated the reaction between several substituted nitrobenzenes and sodium ditelluride in DMF. Among these were some *m*- and *p*-chloro derivatives. Both were found to yield the azo compounds without nucleophilic displacement of the halide. It is interesting to note in the work reported herein, that in the reaction between *o*-halonitrobenzenes and sodium ditelluride in DMF there occurs an aromatic nucleophilic displacement of the halide together with deoxygenation of the nitro group and ring closure to the phenazine.

Before proceeding to a presentation and discussion of other experimental observations, we wish to report that nitrobenzene, nitrosobenzene, and azoxybenzene all underwent reaction with Na_2Te_2 in DMF to yield the same product, viz., azobenzene. This confirms the observation of Suzuki et al.5)

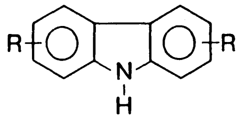
Phenazine was unequivocally identified by its mp, 175 °C, elemental analysis, and ^{13}C NMR spectrum: δ 130.2 ($C_{1,4}$), 129.5 ($C_{2,3}$), and 143.3 (C_{11}). The yields of phenazine were generally of the order of 25—35%. Phenazine was readily identified (GC/MS, comparison with retention time and m./c. of known standard) as the major product formed in the reaction between sodium ditelluride in DMF with *o*-chloro, *o*-bromo, *o*-iodonitrobenzene.

When 4-chloro-3-nitroanisole was used as the substrate the major product was 3,7-dimethoxyphenazine. Similarly, 4-chloro-3-nitro-1-(trifluoromethyl)benzene, as observed from GC/MS data, gave 3,7-bis(trifluoromethyl)phenazine as the major product [(major mass peak at 316)].

Of unusual interest is the evidence for the formation of biphenylenes **1** and carbazoles **2**. The formation of biphenylene as one of the products was confirmed in the case of the reaction between *o*-chloronitrobenzene and sodium ditelluride in DMF. The residue remaining after removal of the solids (including phenazine) was subjected to GC/MS. A strong molecular ion at 152 was observed. The experiment was repeated, first using an authentic sample of biphenylene to establish retention time, peak shape, and location, and second with the addition of a small amount of biphenylene to the reaction residue. The retention times and peak shapes and locations were completely superimposable.



1
R=$-H$, $-CF_3$, $-OCH_3$



2
R=$-H$, $-CF_3$, $-OCH_3$

Strong molecular ion peaks were observed for the indicated molecular ions **1** and **2** when *o*-bromo-, *o*-iodonitrobenzene, 4-chloro-3-nitroanisole, or 4-chloro-3-nitro-1-(trifluoromethyl)benzene were used as substrates in the reaction with Na_2Te_2. However, the identification of the peaks was not corroborated in these cases by comparison with authentic samples.

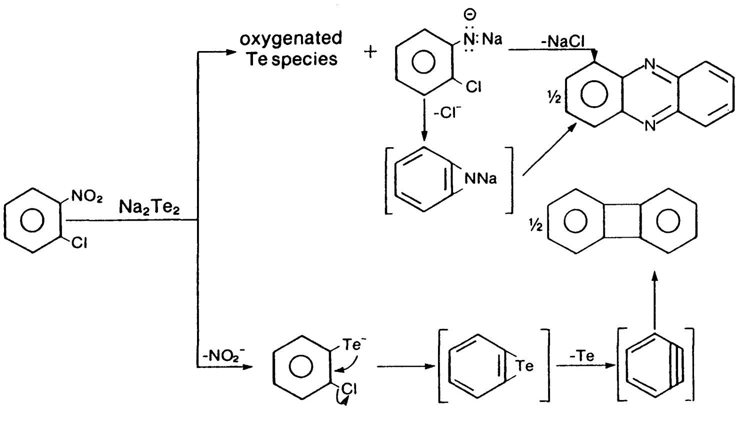
The results of other experiments performed for the purpose of elucidating the nature of the reaction are summarized below.

a. The reaction between 4-chloro-3-nitroaniline and Na_2Te_2 in DMF gave 2,2′-dinitro-4,4′-diaminobiphenyl as the main product. No reduction of the nitro groups was observed.

b. No evidence of formation of phenazine was noted in the reaction between 2-chloroaniline and Na_2Te_2 in DMF.

c. Equimolar quantities of *o*-chloronitrobenzene and 4-chloro-3-nitroanisole were allowed to undergo reaction with Na_2Te_2 in DMF. The major product, as determined from GC/MS studies was methoxyphenazine, but both phenazine and dimethoxyphenazine were also formed. These results are not quantitative because authentic samples of the methoxyphenazines were not used. However, they clearly suggest the occurrence of a bimolecular condensation.

d. Solutions containing Na_2Te_2 and *o*-chloronitro-



Scheme 1.

benzene in DMF were measured, during the course of the reaction, for paramagnetic susceptibility. No evidence of paramagnetism was observed. This, however, does not rule out the possibility for the formation of free radical species since the measurement is not sufficiently sensitive.

e. The grey residue formed from the reaction between Na_2Te_2 and *o*-chloronitrobenzene was separated under oxygen-free conditions and was found to contain 16.5% oxygen (by fast neutron activation analysis). This gives evidence for the deoxygenation of the nitro group, but does not establish the actual chemical form of the oxygen-containing species.

The observed reactions are exceedingly complex. They are difficult to study mechanistically because of the formation and persistence of the tellurium-rich solid phase. While experimental evidence for a detailed mechanism is lacking, product formation does suggest some reasonable possibilities.

The observation of Suzuki and co-workers on the reduction of aromatic nitro compounds to diazo derivatives by Na_2Te in DMF has already been referred to.[5] This group of investigators has also observed the displacement of the nitro group by NaHTe in ethanol.[5,6] In the present study the ditelluride ion is involved in halide displacement and reduction and elimination of the aromatic nitro group ortho to a halogen. The anionic tellurium species presumably function as deoxygenating agents and, as previously indicated,[5,6] are able to displace the nitro groups. An additional example of the displacement of a nitro group by a nucleophile has been reported by Loudon[7] who observed the conversion of 3,4-dinitro-1-chlorobenzene to 3-phenylthio-4-nitro-1-chlorobenzene by treatment with thiophenol.

In the mechanisms proposed in Scheme 1, the formation of diphenylenes is strongly indicative of a benzyne intermediate. One likely possibility, not shown in the scheme, involves the initial nucleophilic displacement of chloride by Te_2^{2-}. Deoxygenation can then be accomplished either by the ring substituted tellurium or by unreacted ditelluride in the reaction medium.

Experimental

Melting points were determined in capillary tubes on a Büchi-SMP 20 melting point apparatus and are uncorrected. Gas chromatographic/mass spectroscopic (GC/MS) measurements were performed on the Hewlett-Packard model 5995C instrument. Nuclear magnetic resonance spectroscopic measurements were performed on the Varian XL-200 instrument. *N,N*-Dimethylformamide (DMF), was stirred with KOH and distilled from BaO (bp 152 °C). Powdered tellurium (99.9% purity) was obtained as a gift from the Selenium-Tellurium, Assn., Inc. Organic reagents were purchased from the Aldrich Chemical Co. and were used as received.

Preparation of Disodium Ditelluride. All reactions were carried out under an atmosphere of nitrogen or argon. Reactions were carried out in the dark or under a red light. The procedure followed was that described by Sandman et al.[8] Powdered tellurium (15.24 g, 0.19 mol) was placed in a three-necked flask (300 ml) containing 100 ml of dried DMF. A thermometer was inserted through one of the necks, another was sealed with a rubber septum, and to the other was attached a reflux condenser. Metallic sodium (2.73 g, 0.119 mol) in 100 ml of DMF was added and the mixture was heated slowly, with continuous magnetic stirring, until it reached a temperature of 110 °C. The reaction can be quite violent at the mp of sodium (ca. 97 °C) and slow, gradual heating is desirable. The mixture was stirred for 1 h at 110 °C and then allowed to cool to 55 °C. The solution is deep purple in color.

Reaction of Aromatic Nitro Compounds with Excess Na_2Te_2. The reactions were carried out using a three-to four-fold excess of Na_2Te_2. A solution of the reagent in 100 ml of DMF was added to the Na_2Te_2 in DMF through the rubber septrum and the mixture was stirred for 23 h at 50 °C. The solution was then filtered under nitrogen and the precipitate was washed with 80 ml of hot DMF. The filtrate was evaporated under reduced pressure. The solid or heavy viscous liquid that remained was then taken up in an appropriate solvent, usually benzene, and allowed to crystallize in the cold. Isolated crystalline solids were recrystallized from appropriate solvents until reproducible mp's were obtained. In those cases where the residual oils were formed, solutions in appropriate solvents, usually benzene, were taken for GC/MS measurements. Details of a specific experiment are given in the next paragraph.

A solution of disodium ditelluride was prepared according to the method previously described from 15.30 g, 0.119 mol of powdered tellurium and 2.78 g, 0.121 mol of sodium in 200 ml of DMF under an atmosphere of nitrogen. The solution was cooled to 60 °C and to it was added with magnetic stirring, through the attached rubber septum, a solution containing 5.15 g, 0.0275 mol of 4-chloro-3-nitroanisole. The temperature jumped to 98 °C upon the addition of the anisole. The mixture was stirred for 20 h at 35 °C. The mixture was filtered, under nitrogen, and the filtrate was evaporated under reduced pressure with heating (external hot water bath) to a viscous dark syrup. This was refluxed with 200 ml dry benzene containing decolorizing charcoal, filtered and again taken to a viscous syrup under reduced pressure. Storage in a refrigerator overnight showed the presence of a crystalline solid. This was recrystallized from ethanol/chloroform in the presence of decolorizing charcoal which was removed by filtration. The final product, green crystals of 3,7-dimethoxyphenazine were obtained in yields of 24, 30, and 37% on three different runs (based on recrystallized material). The recrystallized solid melted at 251—253 °C: A low resolution mass spectral peak corresponding to the molecular ion was observed at 240.17; for $C_{14}H_{12}N_2O_2$. Calcd (Found): C, 69.99 (70.07); H, 5.03 (5.11); N, 11.65% (11.65%); the ^{13}C NMR spectrum showed resonances at δ 55.8 assigned to -OCH_3 at δ 160.2 assigned to quaternary ring carbons attached to methoxy groups (C_3 and C_7) and at δ 143.4 and 140.4 (quaternary carbons attached to ring nitrogen atoms). Resonances at δ 129.9 and 125.9 are assigned to ring carbons $C_{2,6}$ and $C_{4,8}$ and at δ 104.9 to ring carbons $C_{1,5}$, but this group of assignments cannot be made unequivocally.

The financial assistance of the Robert A. Welch Foundation in support of this work is gratefully acknowledged.

References

1) N. L. M. Dereu, R. A. Zingaro, E. A. Meyers, and M. Renson, *Organometallics*, **1**, 111 (1982).

2) E. A. Meyers, N. L. M. Dereu, and R. A. Zingaro, *Cryst. Struct. Commun.*, **10**, 1353 (1981).

3) a) M. T. Bogert and A. Stull, *J. Am. Chem. Soc.*, **49**, 2011 (1927); b) H. Suzuki and M. Inouye, *Chem. Lett.*, **1985**, 1671.

4) R. A. Zingaro, C. Herrera, and E. A. Meyers, *J. Organomet. Chem.*, **306**, C36 (1986).

5) H. Suzuki, H. Manabe, T. Kawaguchi, and M. Inouye, *Bull. Chem. Soc. Jpn.*, **60**, 771 (1987).

6) A. Osuka, H. Shimizu, and H. Suzuki, *Chem. Lett.*, **1983**, 1373.

7) J. D. Loudon, *J. Chem. Soc.*, **1939**, 902.

8) D. J. Sandman, J. C. Stark, and B. M. Foxman, *Organometallics*, **1**, 739 (1982).