*Journal of Organometallic Chemistry*, 168 (1979) 163—165

# PHOTO-$S_{RN}1$ REACTIONS OF PHENYL TELLURIDE ANION WITH HALOARENES

ADRIANA B. PIERINI and ROBERTO A. ROSSI

*Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Est. 32, 5000 Córdoba (Argentina)*

(Received August 21st, 1978)

## Summary

Phenyl telluride anion was prepared in liquid ammonia by reaction of diphenyl ditelluride with two equivalents of sodium metal under nitrogen. This anion reacts with haloarenes under irradiation to form aryl phenyl tellurides, probably by the photo-$S_{RN}1$ mechanism of aromatic substitution.

---

Recently we reported the reaction of the phenyl selenide anion with haloarenes by the photo-$S_{RN}1$ mechanism of aromatic substitution [1]. In view of the similar chemistry of selenium and tellurium compounds, we decided to study the photostimulated reaction of the phenyl telluride anion with haloarenes in liquid ammonia.

We prepared the phenyl selenide anion by means of the acid—base reaction of benzeneselenol with potassium or sodium t-butoxide in liquid ammonia, and also by cleavage of diphenyl diselenide with sodium metal in liquid ammonia. In the second method we added diphenyl diselenide to dry liquid ammonia under nitrogen and then small pieces of sodium metal until the blue color of the solvated electron persisted for at least 15 min. Approximately two equivalents of sodium were consumed per mol of diphenyl diselenide as required by reaction 1.

$$\mathrm{PhSeSePh} + 2\ \mathrm{Na} \xrightarrow{\mathrm{NH_3}} 2\ \mathrm{PhSe^-\ Na^+} \qquad (1)$$

Since it was easier and cleaner to work with the diselenide than with benzeneselenol, we prepared the phenyl telluride anion from diphenyl ditelluride and sodium metal in liquid ammonia. Previously the phenyl telluride anion had been prepared by cleavage of diphenyl ditelluride with lithium metal in THF [2].

When we added sodium to diphenyl ditelluride in dry liquid ammonia under nitrogen, we noted that even after addition of more than two equivalents of sodium the blue color of the solvated electrons did not persits. Approximately four equivalents of sodium per mole of diphenyl ditelluride were necessary to obtain a blue solution with the color persisting for 15—20 min. After quenching and work-up of the reaction mixture we found benzene in 88% yield (by GLC with toluene as internal standard) and a black residue that was not investigated further.

In the reaction of diphenyl diselenide such behavior was not encountered, indicating that phenyl selenide anion did not react with solvated electrons in excess. The appearance of benzene as a product in the reaction of diphenyl ditelluride with solvated electrons indicated either that the phenyl telluride anion reacts with solvated electrons in excess giving ultimately benzene, or that the cleavage occurs in some other way and not through the phenyl telluride anion. In order to check if phenyl telluride anion is an intermediate in this reaction, we added exactly two equivalents of sodium metal to diphenyl ditelluride in liquid ammonia, and then an excess of methyl iodide in order to trap any phenyl telluride anion formed. After work-up, we found 8% benzene (by GLC) and isolated pure phenylmethyl telluride in 80% yield (structure confirmed by NMR). These results indicate that the phenyl telluride anion is indeed an intermediate in this reaction.

The behavior of the Group VIA anions of structure $PhX^-$ (X = O, S, Se and Te) resembles the behavior of the Group VA anionic compounds $Ph_2Y^-$ (Y = P, As, Sb and Bi) [3]. In both series the metal—carbon bonds of the species with the heaviest element (X = Te, Y = Bi) are cleaved by alkali metals in liquid ammonia.

The photostimulated reaction of iodobenzene with phenyl telluride anion in liquid ammonia [prepared from diphenyl ditelluride and sodium (1/2 molar ratio)] produced, after 220 min irradiation with two 250 W high pressure UV lamps (Philips, Model HTP), iodide ion in quantitative yield (determined by potentiometric titration) and diphenyl telluride in 90% yield (isolated as diphenyltellurium dibromide) [4]. The results of the reactions with other haloarenes are

TABLE 1

PHOTOSTIMULATED REACTIONS OF HALOARENES WITH PHENYL TELLURIDE ANION IN LIQUID AMMONIA [a]

| ArX | mmoles | $(PhTe)_2$ (mmoles) | Na metal (mmoles) | Time [b] (min) | Yield (%) [c] | |
|---|---|---|---|---|---|---|
| | | | | | $X^-$ | ArTePh |
| Bromobenzene | 6.88 | 3.44 | 6.91 | 220 | 24 | [d] |
| Iodobenzene | 7.93 | 3.90 | 7.87 | 220 | 100 | 90 [e] |
| 1-Chloronaphthalene | 7.71 | 3.85 | 8.04 | 220 | 60 | 37 |
| 1-Bromonaphthalene | 6.38 | 3.19 | 6.70 | 60 [f] | 1 | 0 [g] |
| 1-Bromonaphthalene | 6.38 | 3.19 | 6.70 | 60 | [h] | 40 [i] |
| 1-Bromonaphthalene | 6.38 | 3.19 | 6.70 | 220 | 80 | 51 [j] |

[a] Reactions were carried out in ca. 250 ml of dry liquid ammonia under nitrogen. [b] Irradiated in a reactor equipped with two 250 W high-pressure UV lamps (Philips, Model HTP) refrigerated with water. [c] Halide ions determined potentiometrically. The yield of ArTePh represents isolated material. [d] Diphenyl telluride was determined qualitatively by GLC and TIC. [e] Isolated as diphenyltellurium dibromide, identified by m.p. [4] and mass spectrum. [f] Dark reaction, wrapped with aluminium foil. [g] Determined by GLC and TLC. [h] Not determined. [i] Determined by GLC, together with 60% of 1-bromonaphthalene assuming equal molar responses. [j] Isolated as the dibromide and identified by m.p. [6] and mass spectrum.

shown in Table 1. We suggest that the reaction proceeds by the photo-$S_{RN}1$ mechanism of aromatic substitution, as sketched in Scheme 1 [5].

SCHEME 1

$$\mathrm{ArX} + \mathrm{PhTe}^- \xrightarrow{h\nu} (\mathrm{ArX})^{\overline{\cdot}} + \mathrm{PhTe}^\cdot \quad (1)$$

$$(\mathrm{ArX})^{\overline{\cdot}} \rightarrow \mathrm{Ar}^\cdot + \mathrm{X}^- \quad (2)$$

$$\mathrm{Ar}^\cdot + \mathrm{PhTe}^- \rightarrow (\mathrm{ArTePh})^{\overline{\cdot}} \quad (3)$$

$$(\mathrm{ArTePh})^{\overline{\cdot}} + \mathrm{ArX} \rightarrow \mathrm{ArTePh} + (\mathrm{ArX})^{\overline{\cdot}} \quad (4)$$

Electron transfer from phenyl telluride anion to the haloarene occurs in the first step. The haloarene radical anion decomposes to aryl radicals (step 2) and the anion of the leaving group. This aryl radical reacts with the phenyl telluride anion to form a new radical anion (step 3). This radical anion transfers its extra electron to the substrate to give the substitution product (step 4). Steps 2—4 constitute a chain mechanism. The light is necessary since after 60 min of dark reaction with 1-bromonaphthalene there is no change at all, whereas with irradiation for the same period of time the substitution product is formed in 40% yield (see Table 1).

The reactivity of substrates studied shows the usual behavior for this type of reaction, i.e., the reactivity order is iodobenzene > bromobenzene and 1-bromonaphthalene > bromobenzene. A comparative study of the reactivity of the anions $\mathrm{PhS}^-$, $\mathrm{PhSe}^-$ and $\mathrm{PhTe}^-$ with the same haloarenes is in progress.

## Acknowledgments

This research was supported in part by the Consejo Nacional de Investigaciones Cientìficas y Técnicas, Argentina. ABP gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones, Argentina. The mass spectra were run at the University of California, Santa Cruz, and the University of Buenos Aires, Through the courtesy of Professors J.F. Bunnett and E.G. Gross. We thank Professor C.F. Bernasconi for reading the manuscript.

## References

1 A.B. Pierini and R.A. Rossi, J. Organometal. Chem., 144 (1978) C12.
2 K.J. Irgolic, P.J. Busse and R.A. Grigsby, J. Organometal. Chem., 88 (1975) 175, and references cited therein.
3 R.A. Rossi and J.F. Bunnett, J. Amer. Chem. Soc., 96 (1974) 112.
4 W.R. McWhinnie and M.G. Patel, J. Chem. Soc. Dalton Trans., 2 (1972) 199.
5 R.A. Rossi and J.F. Bunnett, J. Org. Chem., 38 (1973) 1407.
6 H.R. Rheinboldt and G. Vicentini, Chem. Ber., 89 (1956) 624.