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ALTERNATIVE SYNTHESES OF DIBENZOTETRASELENAFULVALENE, OF SOME OF ITS PRECURSORS AND OF TETRASELENOALKENES ANALOGS

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Abstract : We report alternative syntheses of dibenzotetraselenafulvalene, of a key presursor and of tetramethylselenoethylene.

"Organic metals" are a research field in constant evolution. The recent[1-2] synthesis of dibenzotetraselenafulvalene and the study of the properties of its charge-transfer salts prompted us to describe our results in this scope.

As shown in scheme 1 we present first a new approach of 1,3-benzodiselenol 2-thione 2a, key molecule for the synthesis of dibenzotetraselenafulvalene 4. The compound 2a can be obtained in two steps through the reaction of benzyne with dimethyl diselenide, and further condensation with thiophosgene at - 80°C. Non symmetrical structure 2b and the fully sulfurated product 2c are available from the corresponding chalcogenides. These chalcogenides can be obtained by the benzyne way[4] (1a, 21 %) or by the tetrafluoroborate intermediate[3] (1b, 42 %). Although the cyclisation yields are rather low[+] 2a : 20 %; 2b : 30 %; 2c : 21 %, our method presents the following advantages : the shortness of the proposed synthesis, the inexpensiveness of the starting materials and the easy possibility to obtain unsymmetrical products 2b.

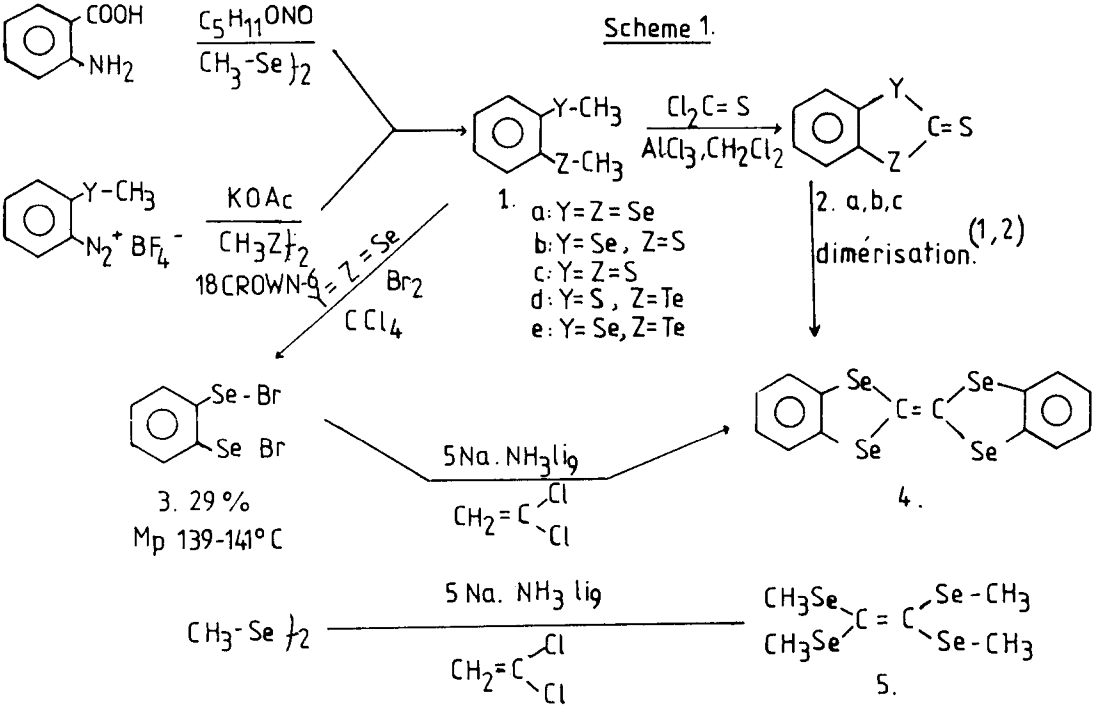
[+] The structure of the isolated pure products has been established by NMR methods (^{1}H and ^{13}C), by mass spectrometry as well as by comparison with the melting point of the known derivatives :

(2a) : 148°C, litt.[1-2] : 147-148°C; (2b) : 130-131°C, litt.[5] : 130-131°C;
(2c) : 162°C, litt.[6] : 164°C.

Heterocycles 2a-c are di-merized through classical method[1,2].

Unfortunately in the tellurium series, we observed a different behaviour in the cyclisation step of the chalcogenides 1d-e. Thiophosgene acts as a chlorinating agent and leads to the corresponding telluronium salts, without cyclisation.

During the course of other synthetic investigations, we observed that dimethyldiselenide condensed with vinylidene chloride to give tetramethylselenoethylene 5 in a 30 % yield (Mp 92-94°C). The reaction mechanism is not yet clear but proceeds probably through an acetylenic intermediate. We have successfully applied the same reaction to the sodium bis-o-benzeneselenolate generated by polarization inversion of the bis(o-benzeneselenenyl)bromide 3, this latter being obtained from 1a. The resulting dibenzotetraselenafulvalene 4 is isolated in a 48 % yield and is identical to the known product[1-2]. This chemical pathway appears to be the more rapid and efficient for the synthesis of 4. We actually investigate it's application to o-dichalcogenoethers 1b-e.



References

1. K. LERSTRUP, M. LEE, F.M. WIYGUL, T.J. KISTENMACHER and D.O. COWAN, J. Chem. Soc., Chem. Commun., 1983, 294.
2. I.B. JOHANNSEN, K. BECHGAARD, K. MORTENSEN and C. JACOBSEN, J. Chem. Soc., Chem. Commun., 1983, 295.
3. A. LUXEN and L. CHRISTIAENS, Tetrahedron Letters, 1982, 3905.
4. The benzyne way gives a lower yield than [3] but is more rapid.
5. H. KENNETH SPENCER, M.V. LAKSHMIKANTHAM, M.P. CAVA and A.F. CARLTO, J. Chem. Soc., Chem. Commun. 1975, 867.
6. E.K. FIELDS and S. MEYERSON, Tetrahedron Letters, 1970, 629.

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