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SYNTHESIS AND REDUCTIVE ELIMINATION OF TRIARYLBIS(PHENYLETHYNYL)ANTIMONY (V)

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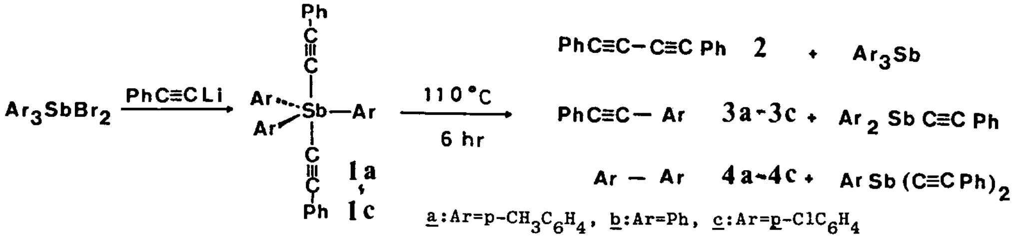
Abstract: Triarylbis(phenylethynyl)antimony (V) (1a-1c) were synthesized from triarylantimony dibromide and lithium phenylacetylide. Thermolytic reductive elimination of 1a-1c took place at 110 °C and the aryl-alkynyl coupling product (3) increased as the aryl group became more electronegative. The result is consistent with the apical-apical coupling from the trigonal bipyramidal structures, which was predicted to be symmetry-allowed by Hoffmann.

The mode of the intramolecular reductive elimination of unsymmetrical pentavalent species has been the subject for discussion in theoretical field.[1-3] According to the Hoffmann's prediction on PH_5,[1] which was supported by Kutzelnigg later,[3] the apical-apical and equatorial-equatorial eliminations from the trigonal bipyramidal structure are symmetry-allowed. Any experimental confirmation of the prediction, however, has not been offered to date, probably due to difficulties in the synthesis of properly substituted unsymmetrical acyclic pentavalent species. In this point of view pentavalent antimony species (SbX_3Y_2) bearing five carbon substituents are suitable for examination of the prediction because they are thermally more stable in comparison with other pnictogen analogues and also reverse reaction, that is, oxidative addition between the resulting species such as SbX_3 and Y_2, does not take place in contrast to the case where Y=halogen.[4] For this purpose we synthesized bis(phenylethynyl)antimony (V) (1a-1c) and examined the substituent effect on the distribution of the ligand coupling products. The compounds 1a-1c were synthesized by a similar method with trimethyldipropynylantimony (1d),[5] that is, lithium phenylacetylide was added to triarylantimony dibromide in THF. The reaction mixture was evaporated, extracted with benzene, and the extract was evaporated again and the residue was crystallized from hexane under nitrogen to give colorless crystals. The purity of 1 was checked by ^1H NMR[6] to be better than 95 %. These compounds are quite unstable to atmospheric moisture, especially 1c is also thermally unstable to avoid enough recrystallization, therefore 1c may contain a small amount of LiBr. However, 1c gave very clear and satisfactory ^1H NMR spectrum.



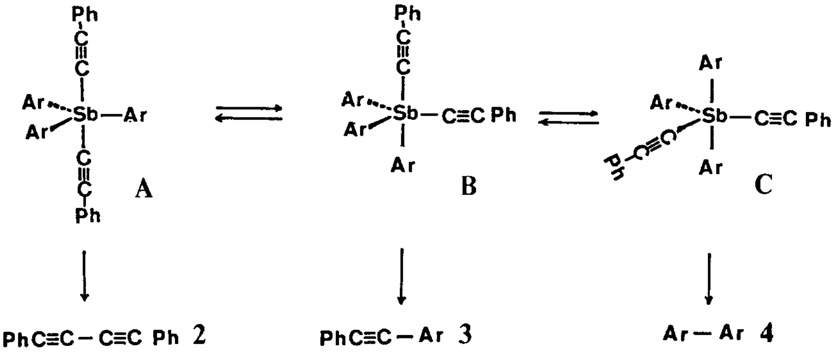
When 1a-1c were heated to 110 °C without solvent, clean reductive elimination occurred to give trivalent antimony compounds and ligand coupling products, which were determined quantitatively by GLC analysis (Table I).[7] In the case of 1c the total yield of the products was rather low probably because of the existence of LiBr but there were no other organic products. Three types of coupling products are expected to be formed a priori but biaryls could not be detected at all. The ratio of aryl-alkynyl coupling increased as the aryl group became more electronegative. The result is interpreted based on the following well-known facts; (i) the structure of **1d** was determined to be trigonal bipyramid by X-ray analysis[5] and such can be taken for granted for **1a-c**, (ii) acyclic pentavalent species are nonrigid in solution, that is, a rapid intramolecular positional exchange of ligands takes place among isomers with the trigonal bipyramidal structures,[8] (iii) isomers with more electronegative substituents in the apical position are preferred (apicophilicity).[9] Thus, the fast equilibration among A-C takes place and the equilibrium shifts gradually to the right in Scheme I as the aryl group becomes more electronegative. In accordance with the experimental result, we can conclude here that the ligand-ligand coupling takes place via apical-apical path due to the weakness of the apical bond, which is consistent with the Hoffmann's prediction. This is certainly the first experimental approach to the theoretical prediction and there can be some other possibility to interpret the result, however the instability of **1** prevents detailed examination and the research on more stable and suitable system is now in progress.

Table 1. Thermolytic Reductive Elimination of **1a**-**1c**.

1	Ar	Ratio PhC≡CC≡CPh	:	PhC≡CAr	:	Ar-Ar	Total Yield (%)[a]
1a	p-$CH_3C_6H_4$	76	:	24	:	0	93
1b	Ph	66	:	34	:	0	99
1c	p-ClC_6H_4	50	:	50	:	0	64

a: GLC yield

Scheme 1



References and Notes

(1) R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Am. Chem. Soc.*, 94, 3047 (1972). (2) J. M. Howell, *J. Am. Chem. Soc.*, 99, 7447 (1977). (3) W. Kutzelnigg and J. Wasilewski, *J. Am. Chem. Soc.*, 104, 953 (1982). (4) H. Hartmann and G. Kuhl, *Angew. Chem.*, 68, 619 (1956). (5) N. Tempel, W. Schwarz, and J. Weidlein, *J. Organometal. Chem.*, 154, 21 (1978). (6) ^{1}H NMR (C_6D_6, δ): **1a**; 2.42 (s, 9H), 6.9-7.2 (m, 12H), 7.4-7.65 (m, 4H), 8.98 (d, 6H, J=9Hz). **1b**; 6.8-7.65 (m, 19H), 8.85-9.20 (m, 6H). **1c**; 6.95-7.23 (m, 12H), 7.36-7.58 (m, 4H), 8.70 (d, 6H, J=8Hz). (7) Pure **2** was obtained by the reductive elimination of **1a-c**. Reference samples of **3** and **4** for quantitative analysis were prepared according to the literatures: **3**: R. D. Stephens and C. E. Castro, *J. Org. Chem.*, 28, 3313 (1963); **4**: P. E. Fanta, *Synthesis*, 1974, 9. (8) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960). (9) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963). (10) Grant-in-aid for Special Project Research (No.61225019) by the Ministry of Education, Science, and Culture is acknowledged for partial support of this research.

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