

present in the solution ('retained activity') increases regularly with the value of the molar ratio [electron donor]: [AlI₃].

The 'exchange blocking' may be attributed to the well-known tendency of the trihalogenides of the aluminium group metals, which are distinct electron acceptors, to the formation of $D \rightarrow MX_3$ complexes, where D is the electron donor molecule². The effect can be explained if one assumes that the exchange of iodine between the alkyl iodide and the $D \rightarrow MI_3$ complex is much slower than the exchange between alkyl iodide and metal iodide. Further investigations are needed to test this assumption.

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¹ Breshneva, N., Roginsky, S., and Shilinsky, N., *J. Phys. Chem. (U.S.S.R.)*, **8**, 848 (1936). Breshneva, N., and Roginsky, S., *ibid.*, **10**, 367 (1937); Breshneva, N., and Roginsky, S., *Usp. Khim.*, **7**, 1503 (1938). Fairbrother, F., *J. Chem. Soc.*, 293 (1941).

² Moeller, T., *Inorganic Chemistry*, 765 (J. Wiley and Sons, New York, 1957).

Preparation of Aluminium Arsenide by a Vapour Phase Transport Reaction

LITTLE work has been reported on the preparation of the semi-conducting compound aluminium arsenide, mainly because of the practical difficulties involved. Preparation from the melt is difficult because of the high melting point of the compound (about 1,700° C) and of the extreme reactivity of aluminium at this temperature. A few workers have prepared small crystals from the melt, and Stambaugh has produced polycrystalline ingots. This work is reviewed in ref. 1. The best of this material has an impurity carrier density of the order of 10¹⁹/cm³ and is *p*-type.

We have prepared aluminium arsenide by an open-tube vapour phase transport method in which aluminium is transported in the presence of arsenic vapour in a stream of hydrogen. Aluminium is transported by the reversible reaction:



in the temperature region 1,150°–1,000° C, and aluminium arsenide is formed either as free-growing crystals or as single crystal epitaxial layers on gallium arsenide substrates.

The material is transparent and orange brown in colour. It is not stable in moist air, quickly developing a 'bloom' on the surface, and slowly crumbling away, but good protection is afforded by dry hydrogen.

Epitaxial layers up to 200μ thick on substrates of 1 cm² area have been grown at rates of 0.4 μ/min. The substrate can be entirely removed by lapping and polishing with diamond paste under kerosene to leave a thin wafer of aluminium arsenide, to which electrical contacts may be made by soldering on gold wires with indium. Hall-effect measurements made on such wafers show them to be *n*-type with carrier densities of about 6 × 10¹⁷/cm³ and mobilities of about 100 cm²/V-sec; compensation is suspected.

Spectrographic analysis has shown the major impurity to be silicon and improvements to the apparatus to eliminate sources of contamination are expected to yield material with a significantly lower carrier density.

Aluminium phosphide has also been prepared by a similar technique as an oriented growth on silicon substrates and as thin pale yellow needles. The conditions

appear to be more critical than for the arsenide and growth rates have been very low.

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¹ Willardson, R., and Goering, H. (eds.), *Compound Semiconductors*, 1, 184 (Reinhold Pub. Corp., New York, 1962).

Characteristics of Benzylic Carbanions

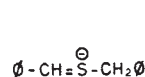
THE formation of a benzylic carbanion from 2-phenylethanethiol in the presence of potassium hydroxide at 200° ultimately yields polystyrene (53 per cent) by a β-elimination of sulphide ion¹. Recently, we have observed that the carbanions formed from benzylsulphide and related species in potassium *tert*-butoxide/dimethylformamide (DMF) at 80° undergo a 1,3-re-arrangement and subsequent β-elimination of the sulphur moiety to yield stilbene² in the same manner as above. As a logical extension of these studies, we have examined the effect of the hetero atom on rearrangement-elimination reactions of this type. The results obtained are of theoretical rather than synthetic interest.

All decomposition studies were carried out in a 1 molar solution of potassium *tert*-butoxide in dimethylformamide at 80° for 20 h. The molar ratio of potassium *tert*-butoxide/reactant was three. The presence or absence of specific products was determined by infra-red, ultra-violet, and gas chromatography (temperature programmed on a 2-ft. silicone rubber column between 75 and 250°) comparison to authentic compounds. Under these conditions, dibenzyl ether gave only 3 per cent yield of stilbene despite the visual evidence of carbanion formation (deep red colour). Further, 1,2-diphenylethanol, 1-phenylethanol, and 2-benzyl-2-propanol did not form any measurable quantity of olefinic products. The latter can be attributed to an equilibrium reaction between *tert*-butoxide ion and the alcohol which leads to alkoxide ions and *tert*-butyl alcohol and to deactivation of the *tert*-butoxide ion by formation of alcohol-KO*t*Bu aggregates. In the former case, β-elimination would require formation:

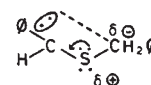


of an oxide ion (O⁼) which is highly unfavourable. Dibenzylamine behaved in a manner similar to dibenzylether and did not form any stilbene after 20 h. In contrast, 1,2-diphenylethyl-*N*-methyl amine afforded stilbene in 42 per cent yield and presumably methylamine. As previously noted, dibenzylsulphide readily undergoes a rearrangement-elimination to stilbene (45 per cent) and hydrogen sulphide in DMF.

When the foregoing results are considered all together one is led to several general conclusions under these reaction conditions. Elimination of sulphide ion proceeds much more readily than elimination of an oxide ion. β-elimination occurs in 1,2-diphenylethyl-*N*-methyl amine because of preferential proton abstraction from the 2-benzyl carbon atom and not from the amino group. Finally, the rearrangement of benzyl sulphide is facilitated not only by *d*-orbital stabilization of the initially formed carbanion (I) but also by the electron donor and accepting properties of:



I



II