then be used in further polymerizations, as for example in a polysulfide condensation. In all cases a heterogeneous distribution of molecular weights is obtained in the preparation of the polymeric dihalides which in the simplest case would be a "random" distribution.[1,2]

The most desirable chain transfer agent to be used in this connection is one whose chain transfer constant is close to unity. In this case the number average and weight average molecular weights should be approximately independent of conversion and the distribution of molecular weights at high conversion should be much less heterogeneous than is the case when the chain transfer constant differs appreciably from unity.

We investigated numerous dihalides as chain transfer agents for styrene polymerization in an attempt to select several whose chain transfer constants were close to unity. The data for chain transfer constant were obtained in most cases at 60° and in some cases at 80°. The experimental procedure used was identical with that reported by Gregg and Mayo[3,4] using intrinsic viscosity to obtain number average degree of polymerization.

To check our experimental accuracy we redetermined the values for the chain transfer constant of carbon tetrachloride with styrene at 60°. Our value was 0.0087 compared with the Gregg–Mayo value[3] of 0.0093.

The following observations should be pointed out: (1) In using the Gregg–Mayo method, it is very necessary to produce polymers of very low conversion. (2) In certain cases we used thermal initiation and in other cases we used benzoyl peroxide as an initiator. The results are independent of the form of initiation. (3) When large quantities of the most active dihalides were used an important retardation of polymerization was observed in the presence or absence of catalyst. (4) The molecular weight distributions to be expected when symmetrical dihalides are used as transfer agents is different from the simpler case when one halogen atom is very active to chain transfer and the other is relatively inert. (5) When dichlorides are used as the transfer agent we believe that very often hydrogen atoms rather than chlorine atoms are abstracted which, of course, does not produce polymers with a chlorine atom at each end. On the other hand, when dibromides or diiodides are used, polystyrene molecules are formed with a bromine or iodine atom at each end. (6) A certain fraction of the chains, corresponding to those that were initiated by catalyst fragments, or possibly by the thermal initiation, have bromine or iodine atoms at only one end. This fraction is small when active chain transfer agents are used in large concentrations. (7) At high conversions important transfer occurs with the halide terminated polymer as well as with the original dihalide molecules.

Table I shows the chain transfer constants for various purified dihalides with styrene obtained under the indicated conditions.

The results indicate that for comparable molecules iodides are more active than bromides and bromides more active than chlorides. Allylic or benzylic halides are exceptionally active, which has been previously noted for hydrocarbons.[4] The halogen atom on an acid halide is also extremely active.

TABLE I

CHAIN TRANSFER CONSTANTS FOR STYRENE WITH VARIOUS DIHALIDES

Dihalide	Temp., °C.	Weight % benozyl peroxide	Chain transfer constant
Bischloroethylformal	80	0.0165	0.00060
Methylene dichloride	80	.0165	.00095
Ethylene dichloride	80	.0165	.00098
1,4-Dichlorobutene-2	80	.0165	.0051
Chloroacetyl chloride	60	None	.330
Methylene dibromide	60	None	.011
p-Xylylene dibromide	60	None	.015
Styrene dibromide	60	None	.195
Stilbene dibromide	60	None	.302
Bromoacetic acid[b]	60	None	.043
Acetyl bromide[a,b]	60	None	.86
Methylene diiodide	60	None	.071

[a] Value somewhat uncertain due to partial hydrolysis. [b] Monohalides.

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(2) R. C. Fettes, A. V. Tobolsky and D. H. Johnson, Plastics Laboratory Report No. 17A, March 15, 1950. Available on request from Plastics Lab., Princeton University.

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Reduction of an Amidine with Lithium Aluminum Hydride

BY R. T. GILSDORF AND F. F. NORD

Because of the structural similarity existing between amidines and amides, interest in the former class of compounds was fostered in these laboratories[1a,b] when reports[2,3] appeared in the literature on the reduction of amides with lithium aluminum hydride. An investigation was undertaken to ascertain whether amidines would behave analogously to amides when similarly treated. Study of the literature revealed that, in general, amidines in the free state are quite prone to hydrolysis to the corresponding amides, thus rendering them unsuitable for comparison with amides since the products could not be established as arising from the reduction of the amidine or the amide generated from the amidine by hydrolysis.

However, one class of amidines, *i.e.*, those which are N,N-disubstituted aromatic derivatives, seem

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to be stable toward hydrolysis. Therefore, a typical representative of this group, N,N-diethylbenzamidine, was subjected to the action of an excess of lithium aluminum hydride, and its reduction was found to be analogous to that of N,N-diethylbenzamide, the former yielding benzylamine, the latter, benzyl alcohol.[2]

Experimental[4]

Benzylamine.—N,N-Diethylbenzamidine (13.5 g., 0.0767 mole) in 50 ml. of absolute ether reacted with lithium aluminum hydride (3.8 g., 0.1 mole) in 200 ml. of absolute ether in the usual way.[2] After the completion of the addition, reflux was continued on the steam-bath for 20 hours. Hydrolysis of the organometallic complex was carried out with 200 ml. of 5% sodium hydroxide. Rectification afforded 1.1 g. (15.4%) of benzylamine, b.p. 60° (7 mm.), and 9.8 g. (72.5%) of N,N-diethylbenzamidine, b.p. 114° (7 mm.).

Phenylthioureide.—The reaction of benzylamine with phenyl isothiocyanate[5] gave the phenylthioureide. The product was recrystallized from 95% ethanol to yield white crystals, m.p. 153–154°, as recorded in the literature.[6]

Anal. Calcd. for $C_{14}H_{14}N_2S$: N, 11.56. Found: N, 11.40.

Picrate.—When benzylamine was treated with picric acid in 95% ethanol, a yellow precipitate was obtained on standing overnight. Washing with 95% ethanol afforded a product of m.p.[7] 194–195°.

Anal. Calcd. for $C_{13}H_{12}N_4O_7$: N, 16.66. Found: N, 16.65.

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(4) All m.ps. and b.ps. are uncorrected.

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Cleavage of Tetraphenylsilane and Benzyltriphenylsilane by Potassium Amide[1]

BY CHARLES R. HANCE AND CHARLES R. HAUSER

It was shown recently[2] that the benzyl-, diphenylmethyl- and triphenylmethyltrimethylsilanes are cleaved by potassium amide in liquid ammonia to form toluene, diphenylmethane and triphenylmethane, respectively. It has now been found that even tetraphenylsilane is cleaved readily by this base, benzene being isolated in 62% yield. The reaction may be represented by equation 1. As with other tetrasubstituted silanes,[2] the mechanism involves presumably the displacement of the hydrocarbon anion from silicon accompanied by the acquisition of a proton from the medium to form the hydrocarbon.

$$(C_6H_5)_3Si{-}C_6H_5 \xrightarrow[NH_3]{K^+NH_2^-} C_6H_6 + \text{silicate} \quad (1)$$

Similarly, benzyltriphenylsilane was cleaved by potassium amide in liquid ammonia, both benzene and toluene apparently being formed. This tetrasubstituted hydrocarbon silane was synthesized in 51% yield from triphenylchlorosilane and benzylmagnesium chloride.

Experimental

Triphenylchlorosilane (practical grade), obtained from Anderson Laboratories, Inc., was purified by distillation at 2 mm. followed by several recrystallizations from benzene and petroleum ether (b.p. 30–60°); the product then melted at 88–90°. Tetraphenylsilane, also obtained from Anderson Laboratories, was recrystallized once from benzene; the product then melted at 231–233°.

Benzyltriphenylsilane.—To a stirred solution of benzylmagnesium chloride (prepared from 0.31 mole of benzyl chloride and 0.29 mole of magnesium) in 500 ml. of anhydrous ether was added 29.4 g. (0.1 mole) of triphenylchlorosilane in 100 ml. of ether. The mixture was refluxed 13 hours and allowed to stand 40 hours. The ether was removed and the residue heated on the steam-bath 11 hours. After adding ether again, the mixture was decomposed with 200 ml. of 25% (by volume) hydrochloric acid. The ether phase was washed several times with water and 10% sodium bicarbonate, dried over anhydrous sodium sulfate, and the solvent removed. The residue was taken up in petroleum ether (b.p. 30–60°) and the solution washed successively with concentrated sulfuric acid, water and 10% sodium bicarbonate. After drying over sodium sulfate, the solution was concentrated to one-fourth its volume to precipitate 17.7 g. (51%) of benzyltriphenylsilane (m.p. 96–98°). Recrystallization from 95% ethanol gave the pure compound melting at 98–99.5°.

Anal.[3] Calcd. for $C_{25}H_{22}Si$: C, 85.68; H, 6.33. Found: C, 85.55; H, 6.40.

Cleavages by Potassium Amide.—Tetraphenylsilane (9.4 g., 0.028 mole) was stirred one hour with 0.0665 mole of potassium amide in 200 ml. of liquid ammonia. After neutralizing the muddy brown mixture with excess (10 g.) ammonium chloride, ether (100 ml.) was added and the ammonia allowed to evaporate. The mixture was filtered and the insoluble salts washed with ether. The filtrate and washings were fractionated through a 30-cm. glass helices-packed column to give 5.4 g. (62%) of benzene boiling at 78–80°, $n^{24}D$ 1.4890; *m*-dinitro derivative, m.p. and mixed m.p. 88–89°. The solid salts were treated with water leaving undissolved a granular material (1.9 g.) which appeared to be an inorganic silicate.

Similarly, benzyltriphenylsilane (3.90 g., 0.0111 mole) was stirred one hour with 0.048 mole of potassium amide in 200 ml. of liquid ammonia. The orange-red mixture was decomposed with ammonium chloride, the liquid ammonia replaced by ether and the mixture filtered. Fractionation of the filtrate gave 0.6 g. of material, b.p. 89–100°, having the characteristics of a mixture of benzene and toluene. None of the original silane was recovered. There was obtained from the solid a granular material (0.5 g.) which appeared to be an inorganic silicate.

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(1) This work was supported by a grant from the Duke University Research Council.

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(3) Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

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The Synthesis of Doubly Labeled Parathion

BY R. E. HEIN AND R. H. MCFARLAND

As an aid in studying the mode of action and metabolism of O,O-diethyl O-*p*-nitrophenyl thiophosphate (parathion), the synthesis of a labeled compound was undertaken. The synthesis of parathion starting with either thiophosphoric trichloride[1] ($PSCl_3$) or phosphorus pentasulfide[2] (P_2S_5) has been described previously. Phosphorus trichloride may also be utilized as a starting material. The direct

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