1 N. S. VYAZANKIN, G. A. RAZUVAEV AND E. N. GLADYSHEV, *Dokl. Akad. Nauk SSSR*, 151 (1963) 1386.
2 W. P. NEUMANN AND K. KÜHLEIN, *Ann.*, 683 (1965) 1.
3 N. S. VYAZANKIN, G. A. RAZUVAEV AND E. N. GLADYSHEV, *Dokl. Akad. Nauk SSSR*, 155 (1964) 830.
4 N. S. VYAZANKIN, G. A. RAZUVAEV, E. N. GLADYSHEV AND T. G. GURIKOVA, *Dokl. Akad. Nauk SSSR*, 155 (1964) 1108.
5 E. WIBERG, O. STECHER, H.-I. ANDRASCHECK, L. KREUZBICHLER AND E. STAUDE, *Angew. Chem.*, 75 (1963) 516.
6 N. S. VYAZANKIN, E. V. MITROPHANOVA, O. A. KRUGLAYA AND G. A. RAZUVAEV, *Zh. Obshch. Khim.*, 36 (1966) 160.
7 N. S. VYAZANKIN, G. A. RAZUVAEV, O. A. KRUGLAYA AND G. S. SEMCHIKOVA, *Dokl. Akad. Nauk SSSR*, 166 (1966) 99.
8 W. SCHLENK, JR., *Dissertation*, Techn. Hochschule, Berlin, 1929, s. 42.
9 D. WITTENBERG AND H. GILMAN, *Quart. Rev. (London)*, 13 (1959) 116.
10 N. S. VYAZANKIN, G. A. RAZUVAEV AND V. T. BYCHKOV, *Isv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1965) 1665.
11 O. H. JOHNSON, *Chem. Rev. (London)*, 48 (1951) 259.
12 A. A. GUNDYREV, N. S. NAMETKIN, G. M. PANTCHENKOV AND A. V. TOPCHIEV, *Investigations in the Field of Organosilicon Compounds*, Akad. Nauk SSSR, Moskow, 1962, p. 205–218.

Received June 6th 1966.

J. Organometal. Chem., 7 (1967) 353–357

Preparation of disulphides from organomercury compounds and sulphur

Current work on aromatic mercuration and transmercuration reactions[1] has led us to study the interaction of organomercury compounds and sulphur. So far, the only investigation in this direction appears to be that of Dreher and Otto[2], who reacted diphenylmercury with sulphur to obtain poor yields of diphenyl sulphide and diphenyl disulphide.

It has now been found that aromatic as well as aliphatic mercury chlorides smoothly react with sulphur in suitable solvents at temperatures of 140–180°. Disulphides (60–75% yield) and mercurous chloride (85–95%) are formed:

$$2\,\mathrm{ArHgCl} + 2\,\mathrm{S} \rightarrow \mathrm{ArSSAr} + \mathrm{Hg_2Cl_2} \qquad (1)$$

Since equilibration of arylmercury salts generally leads to *ortho*-isomers as the main components[1], these isomers are readily available. Reaction with sulphur leads to *ortho*-substituted disulphides which are sometimes difficult to prepare by other routes.

General procedure

About 25 millimoles of the aryl- or alkylmercury chloride and 25 milliatoms of sulphur in 75 ml of purified sulpholan were heated with stirring for 24 h. Mercurous chloride was filtered off and washed with water and acetone. The filtrate was diluted with water and extracted with n-hexane. Column chromatography, using neutral aluminium oxide (Woelm) as the adsorbent and hexane/benzene as the eluent led to pure disulphides. Examples are given in Table 1.

No kinetic measurements were made. Reactivities of the mercury compounds were high for the methoxyphenyl, mesityl and dodecyl derivatives (reaction temperature 140–150°) and lowest for the 2,6-dichlorophenyl compound (reaction

TABLE 1

DISULPHIDES FROM ORGANOMERCURY CHLORIDES AND SULPHUR

Disulphide	*Identification*[a]	*Starting material*
Diphenyl	[b]	C_6H_5HgCl (BDH)
Dimesityl	[b]	2,4,6-$(CH_3)_3C_6H_2HgCl$[c]
Bis(2-fluorophenyl)[d]	B.p. 182°/12 mm; n_D^{20} 1.633[e,f]	*o*-FC_6H_4HgCl[g]
Bis(2-methoxyphenyl)	M.p. 118° (lit.[3] 118–119°)[e]	*o*-$CH_3OC_6H_4HgCl$[h]
Bis(2,6-dichlorophenyl)[d]	M.p. 81–82° (ethanol)[e]	2,6-$Cl_2C_6H_3HgCl$[i]
Di-2-naphthyl	M.p. 138–139° (lit.[4] 139°)[b]	2-$C_{10}H_7HgCl$ (ref. 5)
Di-n-dodecyl	Ref. 6[b]	n-$C_{12}H_{25}HgCl$ (ref. 7)

[a] Infrared and NMR spectra in agreement with literature data as to type and number of nuclear substitutions. [b] M.p. not depressed by admixture with authentic sample. [c] Obtained by direct mercuration of mesitylene with mercuric acetate in acetic acid followed by reaction with NaCl solution. [d] Novel compound. [e] Elemental analysis (C, H and/or S, Cl) checked for disulphide. [f] Isomer purity probably not better than 90%. [g] Obtained from the acetate after transmercuration of C_6H_5F with C_6H_5HgOAc[1]. [h] Obtained as the fluoro compound, starting from anisole. [i] Obtained as the fluoro compound, starting from *m*-dichlorobenzene and taking advantage of the low solubility of the 1,2,3-isomer[1].

temperature of 180–190° required). Sulpholan has an accelerating effect on the reaction; in the case of the mesityl derivative, mesitylene could be used as a solvent.

Mechanism

As for the mechanisms involved, it was first shown that compounds ArSHgCl are unlikely to be intermediates; when heated in sulpholan solution they decomposed only very slowly and, although disulphides were formed, both mercurous chloride and free mercury were obtained.

Substituent effects appear to be polar rather than steric; electron-releasing groups accelerate and electron-withdrawal has a retarding influence. 3-Pyridylmercury chloride fails to give the disulphide.

Dihydroanthracene is dehydrogenated when heated with phenylmercury chloride in sulpholan; however, this reaction is markedly slower than that with sulphur.

Accordingly, the most plausible primary step in the formation of disulphides would seem to consist in an attack by open-chain sulphur radicals ($\cdot S_n^{\cdot}$) on the carbon atom carrying the HgCl group to form an aryl (or alkyl) polysulphenyl radical ($ArS_n^{\cdot}$) with displacement of HgCl. Polar substituent effects would then be interpretable in terms of the well-established electrophilic character of polysulphenyl radicals[8]; the accelerating influence of sulpholan might be due to the polar nature of the transition state.

The present data suggest that the reaction between organomercury chlorides and sulphur is a general one, with the limitation that electron-withdrawing groups may retard or even prevent the formation of disulphides.

Laboratory of Organic Chemistry G. M. LA ROY
University of Leyden (The Netherlands) E. C. KOOYMAN

1 E. C. Kooyman, J. Wolters, J. Spierenburg and J. Reedijk, *J. Organometal. Chem.*, 3 (1965) 487; J. Wolters, Thesis, Leiden, 1965.
2 E. Dreher and R. Otto, *Ber.*, 2 (1869) 542.
3 L. Gattermann, *Ber.*, 32 (1899) 1148.
4 P. T. Cleve, *Ber.*, 21 (1888) 1100.
5 A. H. Blatt (Ed.), *Org. Syn.*, Collective Vol. 2 (1943) 432.
6 A. I. Vogel, *Practical Organic Chemistry*, Longmans, New York, 1957, p. 497.
7 C. S. Marvel, C. E. Adams and R. S. Johnson, *J. Am. Chem. Soc.*, 68 (1946) 2735.
8 W. A. Pryor, *Mechanisms of Sulfur Reactions*, McGraw-Hill, New York, 1962.

Received May 11th, 1966

The overall protium–tritium kinetic isotope effect in the alcoholysis of tri-n-octylaluminum

In recent years a number of investigations have dealt with the determination of the kinetic isotope effect of hydrogen involving the cleavage of metal–carbon bonds. Protium–tritium isotope effects have been described involving reaction of Grignard reagents with alcohols, phenols, and water[1], and of deuterium in the methanolysis of several organometallic compounds[2]. A number of evaluations have been made of the protium–tritium effect in the cleavage of metal–carbon bonds in connection with studies on the mechanism of Ziegler or anionic polymerization[3,4,5], and the overall protium–tritium isotope effect has been determined in the alcoholysis of the reaction products of triethylaluminum with 1-octene[6].

We wish to report on a study carried out to evaluate this effect in the alcoholysis of an aluminum trialkyl, and on the variation of the effect with temperature. Values on temperature effects in the alcoholysis of aluminum alkyls have not been reported in the literature. Our results show that, particularly with isobutyl alcohol, the magnitude of the kinetic isotope effect varies markedly as the temperature is changed. The data suggest cautious use of kinetic isotope effect values, unless the experimental temperatures are well defined.

The alcoholyses were carried out at several temperatures with tri-n-octylaluminum and methanol or isobutyl alcohol containing a trace of tritium in the labile position. The hydrocarbon product was isolated, radioassayed, and the overall kinetic isotope effect, $\overline{k_H/k_T}$, was determined from a comparison with the radioassay of the alcohol used. The results are summarized in Table 1; Arrhenius-type plots of $\overline{k_H/k_T}$ are shown in Fig. 1.

The alcoholysis may be depicted stepwise as

$$R_3Al + R'OH \rightarrow R_2AlOR' + RH \tag{1}$$

$$R_2AlOR' + R'OH \rightarrow RAl(OR')_2 + RH \tag{2}$$

$$RAl(OR')_2 + R'OH \rightarrow Al(OR')_3 + RH \tag{3}$$

with complexing also occurring between the various aluminum compounds as well as with unreacted alcohol. Experiments carried out with stoichiometric amounts of alcohol indicate that reaction (3) is considerably slower than reactión (1) and probably slower than reaction (2). When such stoichiometric reactions were carried out at room temperature, only 56% of the theoretical radioactivity was found in the hydro-