Raman-spektropskopische Untersuchungen, vor allem der Selen- und Tellurverbindungen, sowie die röntgenographische Bestimmung der Bindungswinkel am Chalkogenatom sollen weitere Informationen liefern, die es ermöglichen, die angegebenen Zuordnungen zu sichern und genaue Aussagen über die Strukturverhältnisse in diesen Verbindungen zu machen.

Institut für Anorganische Chemie,
Universität Marburg (Deutschland)
HERBERT SCHUMANN
MAX SCHMIDT

1 J. G. NOLTES, M. C. HENRY UND M. J. JANSSEN, *Chem. Ind. (London)*, (1959) 298.
2 H. KRIEGSMANN UND G. KESSLER, *Naturwissenschaften*, (1960) 393.
3 V. S. GRIFFITHS UND G. A. W. DERWISH, *J. Mol. Spectry.*, 2 (1960) 148.
4 H. KRIEGSMANN UND S. PISCHTSCHAN, *Z. Anorg. Allgem. Chem.*, 308 (1961) 212.
5 H. KRIEGSMANN UND G. KESSLER, *Z. Anorg. Allgem. Chem.*, 318 (1962) 266.
6 H. KRIEGSMANN UND G. KESSLER, *Z. Anorg. Allgem. Chem.*, 318 (1962) 277.
7 H. KRIEGSMANN, H. HOFFMANN UND S. PISCHTSCHAN, *Z. Anorg. Allgem. Chem.*, 315 (1962) 283.
8 R. C. POLLER, *J. Inorg. Nucl. Chem.*, 24 (1962) 593.
9 V. S. GRIFFITHS UND G. A. W. DERWISH, *J. Mol. Spectry.*, 9 (1962) 83.
10 H. KRIEGSMANN UND H. HOFFMANN, *Z. Chem.*, 3 (1963) 268.
11 H. KRIEGSMANN UND H. GEISSLER, *Z. Anorg. Allgem. Chem.*, 323 (1963) 170.
12 H. KRIEGSMANN UND K. ULBRICHT, *Z. Anorg. Allgem. Chem.*, 328 (1964) 90.
13 H. SCHUMANN, K. F. THOM UND M. SCHMIDT, *J. Organometal. Chem.*, 1 (1963) 167.
14 H. SCHUMANN, K. F. THOM UND M. SCHMIDT, *J. Organometal. Chem.*, 2 (1964) 361.
15 H. SCHUMANN, K. F. THOM UND M. SCHMIDT, *J. Organometal. Chem.*, 4 (1965) 22.
16 H. SCHUMANN, K. F. THOM UND M. SCHMIDT, *J. Organometal. Chem.*, 4 (1965) 28.
17 D. H. WHIFFEN, *J. Chem. Soc.*, (1956) 1350.

Eingegangen den 13. Februar 1965

J. Organometal. Chem., 3 (1965) 485–487

Transmercurations effected by monoarylmercury compounds

During investigations on the equilibration of benzene derivatives[1], a new and simple aromatic transmercuration reaction has been observed. For monosubstituted benzenes, this may be formulated as follows:

$$C_6H_5HgX + C_6H_5Z \longrightarrow C_6H_6 + ZC_6H_4HgX \qquad (1)$$

Thus, phenylmercury acetate, nitrate, perchlorate or fluoride were found to react with an excess of many benzene derivatives to produce mixtures of isomeric mercurials. Reaction temperatures of 110–160° and relatively long reaction times (40–2000 h) appeared to be required. Phenylmercury bromide and chloride showed a much lower reactivity, but the exchange of radioactivity reported[2] to take place between C_6H_5HgBr and ^{14}C-labelled benzene is probably due to a transmercuration reaction analogous to (1).

Smooth transmercurations were observed in the case of $Z =$ halogen, NO_2, CN, OCH_3, alkyl, etc., as well as with similarly substituted bifunctional compounds; yields generally exceeded 90 % and only small proportions of polymercurated products were formed. With $Z = OH$, SH, SCH_3, NH_2 and $N(CH_3)_2$, oxidative side reactions predominated. Phenylmercury acetate when heated alone gave benzene and a mixture of polymercurated products, presumably by a type (1) reaction.

J. Organometal. Chem., 3 (1965) 487–489

Working up was done in the usual way, *viz.* by first converting the mercurials to arylmercury chlorides (*e.g.* ZC_6H_4HgCl and C_6H_5HgCl) by means of an aqueous solution of sodium chloride. The HgCl groups were replaced by bromine atoms, using bromine and potassium bromide solution. Aromatic bromides were then analyzed by gas–liquid chromatography and/or infrared spectroscopy, using standard samples of the various pure isomers[1].

Isomer distributions observed appeared to be unusual; they often showed high proportions of *ortho*-isomers (> 60 %), *viz.* for Z = halogen, NO_2, OCH_3. Results so far obtained, some of which are given in the table, indicate that reaction (1) is reversible and is accompanied or followed by equilibration reactions:

$$ZC_6H_4HgX\ (o,m,p) + C_6H_5Z \rightleftarrows ZC_6H_4HgX\ (o',m',p') + C_6H_5Z \qquad (2)$$

In some instances, equilibration has been shown to be complete (*e.g.* with bromobenzene); probably, however, equilibrium has been also attained in most other cases, involving reaction times exceeding 100 hours at 150°. The equilibrated systems display isomer patterns apparently in agreement with recent suggestions[3] concerning substituent effects on equilibria. Thus, high proportions of *ortho*-isomers (Z = halogen, NO_2, OCH_3) may be attributed to dipole–dipole attractions; in the case of *tert*-butylbenzene and biphenyl, the low percentage of *ortho*-isomer is probably due to a steric effect.

As for possible mechanisms, diarylmercury compounds (*e.g.* $C_6H_5HgC_6H_4Z$) are unlikely to be intermediates, since little reaction takes place when diphenylmercury is treated with a molar proportion of acetic acid in the presence of an excess of PhZ under

TABLE I

TRANSMERCURATIONS OF SOME BENZENE DERIVATIVES

Reactants[a]	*Temp.*[b] (°C)	*Reaction time* (h)	*Isomer distributions of* ZC_6H_4HgX[c]		
			% *o*	% *m*	% *p*
$C_6H_5HgOAc + C_6H_5F$	150*	50	20	4	76
$C_6H_5HgOAc + C_6H_5F$	150*	430	86	9	5
$C_6H_5HgOAc + C_6H_5Cl$	132	95	54	23	23
$C_6H_5HgOAc + C_6H_5Cl$	132	430	60	25	15
$C_6H_5HgOAc + C_6H_5Br$	156	40	61	26	13
$C_6H_5HgOAc + C_6H_5Br$	156	150	65	25	10
m-$BrC_6H_4HgOAc + C_6H_5Br$	156	575	65	25	10
$C_6H_5HgOAc + C_6H_5CH_3$	111	1600	37	37	26
$C_6H_5HgOAc + C_6H_5C_6H_5$	150	25	24	34	42
$C_6H_5HgOAc + C_6H_5C_6H_5$	150	350	9	55	36
$C_6H_5HgOAc + C_6H_5NO_2$	150	355	57	28	15
$C_6H_5HgF + C_6H_5Br$	150	380	78	16	6
$C_6H_5HgNO_3 + C_6H_5Br$	150	315	77	17	6
m-$BrC_6H_4HgOAc + C_6H_6$	150*	455	Mainly C_6H_5HgOAc		
Direct mercurations[d]					
$Hg(OAc)_2 + C_6H_5CH_3$	111	1.5	41	21	37
$Hg(OAc)_2 + C_6H_5NO_2$	150	2.5	53	32	15

[a] Molar intake ratios 1:40. [b] Runs marked with an asterisk (*) were done in sealed tubes, the others at atmospheric pressure. [c] Determined via conversions into ZC_6H_4Br. [d] Taken from ref. 6; molar intake ratios about 1:15 and 1:5, respectively.

the conditions of the transmercuration reaction. A four-centre type process involving the mercury atom as the electrophile and the phenyl group as the proton acceptor therefore seems more plausible. Thus, the data for fluorobenzene and biphenyl suggest that the primary step (1) leads to the usual *para–ortho*-isomer patterns of electrophilic substitution; subsequently, these patterns change as a result of equilibration (2).

The present findings strongly suggest that the discrepancies often observed[4,5,6] in direct mercurations carried out in non-aqueous systems—*e.g.* by means of mercuric acetate—are at least partly due to transmercuration–equilibration reactions (2) following the formation of the arylmercury acetates. (*Cf.* the data given in the last two rows of the table.)

Kinetic as well as preparative studies on these new reactions are in hand in this Laboratory.

Laboratory of Organic Chemistry,
University of Leiden,
Leiden (The Netherlands)

E. C. KOOYMAN
J. WOLTERS
J. SPIERENBURG
J. REEDIJK

1 E. C. KOOYMAN AND R. LOUW, *Rec. Trav. Chim.*, 81 (1962) 365; R. LOUW AND E. C. KOOYMAN, *Rec. Trav. Chim.*, 82 (1963) 616; G. J. P. AUGUSTIJN, E. C. KOOYMAN AND R. LOUW, *Rec. Trav. Chim.*, 82 (1963) 965.
2 I. A. KORSHUNOV, *et al.*, *Zh. Obsch. Khim.*, 29 (1959) 1992.
3 E. C. KOOYMAN, *Pure Appl. Chem.*, 7 (1963) 193.
4 W. J. KLAPPROTH AND F. H. WESTHEIMER, *J. Am. Chem. Soc.*, 72 (1950) 4461.
5 G. H. WILLIAMS, *Homolytic Aromatic Substitution*, Pergamon Press, Oxford, 1960, chapter 7.
6 M. MALAIYANDI, H. SAWATZKY AND G. F. WRIGHT, *Can. J. Chem.*, 39 (1961) 1827.

Received March 18th, 1965

The tetraalkylammoniumhalide-catalyzed redistribution of hydrogen and chlorine on silicon

The redistribution of ligands attached to silicon offers a synthetic route to many organochlorosilicon hydrides. Of particular use and interest are catalysts which allow redistribution of silanic hydrogen and chlorine without altering the carbon ligands attached to silicon[1]. Whitmore, Pietrusa, and Sommer[2] found that aluminum chloride, under mild conditions, favored hydrogen–chlorine exchange.

$$Et_3SiH + Et_2SiCl_2 \longrightarrow Et_3SiCl + Et_2SiHCl + Et_2SiH_2$$

Dolgov, Voronkov, and Borisov[3,4,5] and Gilbert, Cooper, and Shade[6] later used this method in the synthesis of organomonochlorosilanes and organodichlorosilanes. As aluminum chloride is also an effective catalyst for the redistribution of silanic hydrogen with alkyl or aryl groups[7], careful control of catalyst concentration and temperature is required to avoid complicating side reactions[3,4,6]. Isomerization of alkyl groups with aluminum chloride has also been noted[5].

A number of nitrogen bases, including dialkylcyanamides and nitriles, were