

MERCURY EXCHANGE BETWEEN DIPHENYLMERCURY AND BIS(*p*-CHLOROPHENYL)MERCURY*

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SUMMARY

Experimental methods for investigating mercury exchange between diphenyl mercury and bis(*p*-chlorophenyl)mercury have been evaluated and kinetic parameters determined using a novel partition technique. An octahedral transition state has been proposed. The investigation was complicated by a relatively fast reaction rate, and the kinetic interference of impurities or hydrolysis products.

INTRODUCTION

The homogeneous interactions of organomercuric compounds have been widely investigated^{1,2} because of their importance in elucidating the mechanism of electrophilic substitution at a saturated carbon atom.

Ingold¹ considered all possible reactions of the type:



where R was an organic radical and R', R'', R''' were either organic or inorganic radicals. He concluded that only a limited number of these substitutions could occur, namely the "one alkyl" (R', R'', R'''-Inorganic), "two alkyl" (R', R'''-Inorganic, R''-Organic) and "three alkyl" (R' Inorganic, R'', R'''-Organic) exchanges. Investigations, employing optically active *sec*-butyl substituted organomercury compounds and radioactive mercury labels, demonstrated that the substitutions occurred via bimolecular (S_E2) or unimolecular (S_E1) mechanisms³. A further, cyclic transition state (S_Ei) has been proposed for some electrophilic substitutions⁴. On theoretical grounds Ingold¹ rejected the possible occurrence of four alkyl exchange reactions of the following type:-



Subsequent work has revealed that redistribution reactions of type (a) can occur between dialkyl mercury derivatives. The reactions were conducted at high tempera-

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tures in sealed vessels and in the absence of solvent or catalyst⁵. The reaction mechanisms were not elucidated, but the vigorous reaction conditions required indicated that a radical process was involved. Recently Reutov *et al.*⁶ have investigated the four alkyl exchange reactions of diphenyl mercury with a variety of reactive organomercuric compounds, such as $(C_6H_5C\equiv C)_2Hg$, $(EtOCCCClF)_2Hg$ and $Hg(CN)_2$. In those cases where reaction was observed, the unsymmetrical reaction product was obtained [type (a)]. In that one of the reactants was a relatively reactive species, these reactions were more akin to the two alkyl exchange reactions between a dialkylmercury compound and a mercuric salt.

Reutov *et al.* have also noted the equilibration of radioactive mercury between diphenyl mercury and bis(*p*-chlorophenyl)mercury⁷ and a number of the similar systems⁸. The reaction mechanism was not elucidated, but in the absence of new reaction products the exchange conformed to type (b).

This report is concerned with establishing usable experimental techniques to elucidate more information on these "four aryl" exchange reactions, with particular reference to the diphenyl mercury-bis(*p*-chlorophenyl)mercury exchange.

EXPERIMENTAL

Materials

Diphenylmercury (J. Sas & Co. Ltd.) was recrystallised three times from benzene and dried at 60° for 15 min and stored over calcium chloride at reduced pressure in the dark. M.p. 122–124° (lit. m.p. 122°^{9a}, 125–126°^{9b}, 122–124°^{9c}). Bis(*p*-chlorophenyl)mercury was prepared by a modification of the method of Dessy and Lee^{10a}. 80% of the stoichiometrically required quantity of dry mercuric chloride in a minimum of anhydrous tetrahydrofuran was slowly added to refluxing (*p*-chlorophenyl)magnesium bromide in dry ether via a dropping funnel. The reaction was refluxed for 10 h and then extracted with an equivalent volume of aqueous 0.2 *N* ammonium chloride to remove the excess of reagent. Evaporation, extraction and recrystallisation from benzene yielded the product. M.p. 251–252° (lit. m.p. 242–243°^{10b}, 249–252°^{10a}). (Found: C, 34.36; H, 1.90. $C_{12}H_8Cl_2Hg$ calcd.: C, 34.03; H, 1.91%.)

Phenylmercuric chloride, phenylmercuric acetate (Kochlight) and phenylmercuric hydroxide (Aldrich Chemicals) were recrystallised from ether, benzene and hot water respectively. Phenylmercuric benzonate was prepared from a suspension of phenylmercuric hydroxide and benzoic acid in acetone and recrystallised twice from chloroform. M.p. 95–97° (lit. m.p. 95–97°^{11a}, 98–99°^{11b}). Phenylmercuric phenolate was similarly prepared from a suspension of phenylmercuric hydroxide and phenol. M.p. 135–136° (lit. m.p. 133–135°¹²).

Solvents

All solvents were fractionally distilled prior to use, with the exception of chloroform, benzene, xylene and tetrahydrofuran which were dried over calcium chloride and then sodium wire before distillation. Pyridine was dried over potassium hydroxide and then fractionally distilled.

Labelled compounds

Mercury-203 was introduced into the organomercuric compounds by the

heterogeneous exchange between stirred radioactive mercury (0.3 mCi of ^{203}Hg in 500 g of mercury) and a saturated solution of the requisite compound¹³. Mercury-203, a ($\beta\gamma$) emitter, was measured as a γ emitter using a well type sodium iodide scintillation counter. (Panax Equipment Limited γ -160).

Analytical procedures

Preliminary examinations of the exchange of label between diphenylmercury and bis(*p*-chlorophenyl)mercury were conducted either by precipitating the least soluble of the reactants from solution or by extracting the most soluble component from solid reaction mixture.

The rate of exchange was determined by equilibrating the reaction mixture in a two phase liquid-liquid system consisting of 5.0 ml of the pyridine reaction mixture, 5.0 ml of cyclohexane and 0.5 ml of water. Providing the reactants possessed sufficiently different partition coefficients in the system, then the gross partition coefficient measured for the equilibration of the radioactive label between the layers was shown to be a function of the individual partition coefficients of the reactants and the specific activity of each layer related to the extent to which the exchange had occurred for the particular reaction sample. In the simple case where there were no new reaction products arising during the exchange of radioactive label between compounds X and Y, the fraction of the reaction (F) that had occurred at time t after the initiation of the reaction may be derived thus:

Let P_X and P_Y represent the partition coefficients of reactants X and Y equilibrated between layers A and B of the system.

$$P_X = \frac{V_A \cdot S_X^B}{V_B \cdot S_X^A} \quad (1)$$

and

$$P_Y = \frac{V_A \cdot S_Y^B}{V_B \cdot S_Y^A} \quad (2)$$

where V_A and V_B are the volumes of layers A and B, and S_X^A , S_X^B , S_Y^A , and S_Y^B represent the measured radioactivities of compounds X and Y in layers A and B respectively.

Further if S_X and S_Y represent the total measured radioactivities of compounds X and Y for a given reaction sample, then

$$S_X = S_X^A + S_X^B \quad (3)$$

and

$$S_Y = S_Y^A + S_Y^B \quad (4)$$

Similarly the total measured activity in each layer, S_A and S_B , is the sum of the activities of the individual components in that layer:

$$S_A = S_X^A + S_Y^A \quad (5)$$

and

$$S_B = S_X^B + S_Y^B \quad (6)$$

Combining (1) and (2) in (6) yields:

$$S_B = \frac{V_B}{V_A} \cdot (P_X \cdot S_X^A + P_Y \cdot S_Y^A) \quad (7)$$

Then (7) - V_B/V_A (5), where $P_X(V_B/V_A)$ is a constant yields:

$$S_Y^A = \frac{S_B - S_A \cdot P_X \cdot (V_B/V_A)}{V_B/V_A \cdot (P_Y - P_X)} \quad (8)$$

In practise the radioactivity per millilitre of each layer is determined.

$$\therefore S_A = C_A \cdot V_A \quad \text{and} \quad S_B = C_B \cdot V_B$$

where C_A and C_B are count rates.

Substituting in (8) and combining with (2):

$$S_Y^B = \frac{V_B \cdot P_Y (C_B - P_X \cdot C_A)}{P_Y - P_X} \quad (9)$$

Similarly substituting in (8) and combining with (9) and (4):

$$S_X = \frac{(V_A + V_B \cdot P_Y) \cdot (C_B - P_X \cdot C_A)}{P_Y - P_X} \quad (10)$$

The fraction of reaction F that has occurred at time t is equivalent to $S_Y/S_{Y\infty}$, where $S_{Y\infty}$ is the activity of component Y at equilibrium. Therefore

$$-\log(1-F) = -\log\left(1 - \frac{S_Y}{S_{Y\infty}}\right) = \frac{(C_{B\infty} - C_B) - P_X \cdot (C_{A\infty} - C_A)}{(C_{B\infty} - P_X \cdot C_{A\infty})} \quad (11)$$

The reaction was also analysed by thin layer chromatography, on 1.0 mm silica gel (silica gel "G") plates, with benzene as the eluent. The plates were visualised by exposing to hydrogen chloride and spraying with a dilute solution of dithizone in chloroform.

RESULTS

Diphenylmercury-bis(p-chlorophenyl)mercury system

Preliminary investigations. A pyridine solution of labelled diphenylmercury (0.08 mole·l⁻¹) and unlabelled bis(p-chlorophenyl)mercury (0.32 mole·l⁻¹), was equilibrated at 60° for 6 h. On cooling the initial crop of crystals was isolated and recrystallised from benzene. The melting point of the latter compound (249–251°) indicated that it was bis(p-chlorophenyl)mercury (m.p. 251–252°¹⁰, m.p. diphenylmercury 121–122°⁹). This was confirmed by comparing the IR spectra of the reactants and the isolated material. The specific activity of the isolated material (1030 c·s⁻¹·g⁻¹) compared well with the theoretical value for the occurrence of a four alkyl exchange reaction without the formation of new reaction products. (Theoretical value 1070 c·s⁻¹·g⁻¹. The expected value for a redistribution reaction was 1160 c·s⁻¹·g⁻¹.) A mixed m.p. examination, with the mixture melting over a 50° range, confirmed that the specific activity of the isolated material could not be attributed to the coprecipitation of diphenylmercury. Finally the wide range of published m.ps. for the unsymmetrical (p-chlorophenyl)phenylmercury (190–210°^{14a}, 165–205°^{14b}, 190–215°^{14c}) confirmed that the exchange had occurred without the formation of new reaction products.

The effect of varying the reaction conditions. The distribution of radioactivity under a variety of reaction conditions was examined. The reaction samples were analysed by rapidly removing the solvent under vacuum and extracting the residue with a

minimum of benzene to preferentially dissolve diphenylmercury. The latter was purified by crystallisation and identified conclusively from its m.p. and IR spectrum. The residue from the extraction was similarly crystallised and shown to be bis(*p*-chlorophenyl)mercury.

The exchange was examined in pyridine solution over a range of reactant concentrations ($0.2500 \text{ mole} \cdot \text{l}^{-1}$ to $0.0025 \text{ mole} \cdot \text{l}^{-1}$), reaction temperatures (60° to 4°) and reaction times (6 h to 5 min). In each case an equimolar concentration of the reactants was employed. Even under the mildest conditions the exchange was shown to have attained equilibrium by the time the separation had been achieved.

The exchange was similarly examined in five other solvents: benzene, cyclohexane, diethyl ether, acetone and tetrahydrofuran. Once again equilibrium was shown to have been achieved under the mildest reaction conditions employed ($0.0025 \text{ mole} \cdot \text{l}^{-1}$, 4° , 5 min). Finally the reversibility of this reaction was confirmed in pyridine solution only. Reaction was very fast under the reaction conditions employed ($0.025 \text{ mole} \cdot \text{l}^{-1}$, 33° , 15 min).

Partition study. The rate of exchange of radioactive label was examined in equimolar pyridine solutions at three different reactant concentrations and temperatures (see Table 1 and Fig. 1). The derived rate constant exhibited considerable varia-

TABLE 1

EXCHANGE OF RADIOACTIVE MERCURY BETWEEN DIPHENYLMERCURY AND BIS(*p*-CHLOROPHENYL)MERCURY

Reactant concn. ^b ($\text{mole} \cdot \text{l}^{-1}$)	Temp. ($^\circ\text{C}$)	Rate constant [$\text{mole}^{-1} \cdot \text{sec}^{-1} (\times 10^{-7})$]
0.010	30	0.8
0.010	40	1.1
0.010	60	2.5
0.015	35	7.1
0.020 ^c	35	6.7
0.020 ^d	35	9.5
0.030	35	14.3

^a $\Delta H^* = 10.5 \text{ kcal} \cdot \text{mole}^{-1}$, $\Delta S^* = -52 \text{ kcal} \cdot \text{mole}^{-1}$, $\Delta G^* = 27 \text{ kcal} \cdot \text{mole}^{-1}$, $E_a = 11.1 \text{ kcal} \cdot \text{mole}^{-1}$.

^b Equimolar solutions. ^c Labelled precursor prepared in pyridine solution. ^d Labelled precursor prepared in benzene solution.

TABLE 2

THIN LAYER CHROMATOGRAPHY EXAMINATION OF THE EXCHANGE OF RADIOACTIVE MERCURY BETWEEN DIPHENYLMERCURY AND BIS(*p*-CHLOROPHENYL)MERCURY

Reactant concn. ^a ($\text{mole} \cdot \text{l}^{-1}$)	Reaction time (min)	Temp. ($^\circ\text{C}$)	Band activities (%)			
			R_f 0.94	R_f 0.92	R_f 0.75	R_f 0.63
0.080	360	100	37.0	60.4	1.4	1.1
0.020	60	40	48.6	52.4	2.1	1.9
0.010	5	0	34.5	60.4	1.7	3.4

^a Equimolar solutions.

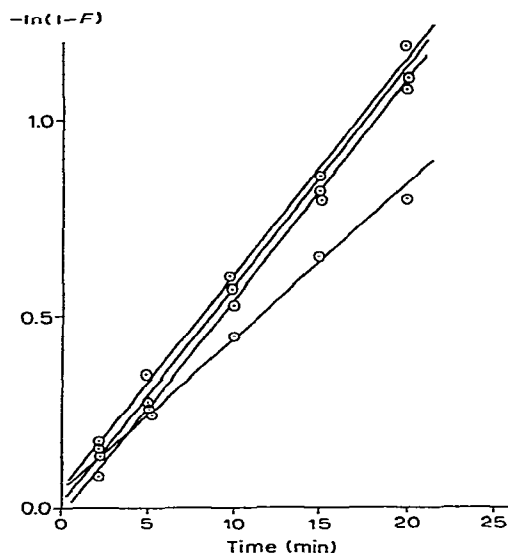


Fig. 1. Exchange of radioactive mercury between diphenylmercury and bis(*p*-chlorophenyl)mercury.

tion when analysed in terms of a bimolecular exchange reaction. It also exhibited some variation with the mode of preparation of the labelled precursor. The activation parameters for the exchange were derived in the usual manner from the observed temperature dependence of the rate constants.

Thin layer chromatography. The distribution of activity between the reactants was further examined by thin layer chromatography. The visualised bands were removed from the plates and the count rate determined. Complete separation of diphenylmercury (R_f 0.90/0.92) from bis(*p*-chlorophenyl)mercury (R_f 0.94) was not achieved. The activity of subsidiary bands was recorded (Table 2).

The interaction of diphenylmercury with phenylmercuric salts

The exchange of radioactive mercury between diphenylmercury and phenylmercuric chloride was examined in pyridine at several different reactant concentrations ($0.080 \text{ mole} \cdot \text{l}^{-1}$ to $0.008 \text{ mole} \cdot \text{l}^{-1}$) by the partition technique, reaction temperatures (100° to 4°) and reaction times (6 h to 5 min). In each case equimolar reactant concentrations were employed. Even under the mildest reaction conditions the exchange was shown to have achieved equilibrium by the time the analysis had been completed. The exchange was analysed by crystallisation and chromatography techniques with the same conclusion. No measurable solvent effect on the exchange rate was detected with benzene, chloroform or tetrahydrofuran. The exchange was shown to be reversible in pyridine solution.

The exchange of radioactive mercury between diphenylmercury and phenylmercuric acetate was similarly shown to have attained equilibrium before separation could be achieved (conditions: pyridine, $0.025 \text{ mole} \cdot \text{l}^{-1}$, 0° , 10 min). The exchange was also studied in benzene and tetrahydrofuran with the same results, and was shown to be reversible in pyridine.

Similarly the exchange between diphenylmercury and phenylmercuric

benzoate, phenylmercuric phenolate or phenylmercuric hydroxide was shown to be equally rapid in an equimolar pyridine solution ($0.025 \text{ mole} \cdot \text{l}^{-1}$, 0° , 10 min).

DISCUSSION

The analysis of the exchange of radioactive mercury between diarylmercury compounds posed considerable experimental problems. Because of the similarity of the reactants a simple separation of the reactants prior to analysis was difficult to achieve. The reactants chosen in this study were the most dissimilar of the known stable diarylmercury compounds. The chloride atoms of the bis(*p*-chlorophenyl)-mercury derivative conferred an enhanced electropositive character upon the central mercury atom, and this difference was sufficient to permit separation of the reactants by crystallisation and extraction. By this laborious method it was possible to establish whether or not exchange had occurred and to examine the nature of any new reaction products. There was a considerable separation error inherent in the method and it could not be employed to establish kinetic and thermodynamic parameters for the exchange. The latter could only be derived by employing the "partition technique" and eqn. (11). This relationship has the advantage of expressing $-\log(1-F)$ in terms of easily measured quantities only. The accuracy of the relationship is determined, in this case, by the standard deviation in the sample count rates and the difference in the individual partition coefficients of the reactants. The greater the difference the more accurate the determination of the rate constant. A separate study demonstrated that there was no inherent significant separation error. This was confirmed by observing that all of the $-\log(1-F)$ vs. time plots passed through the origin, within the experimental error.

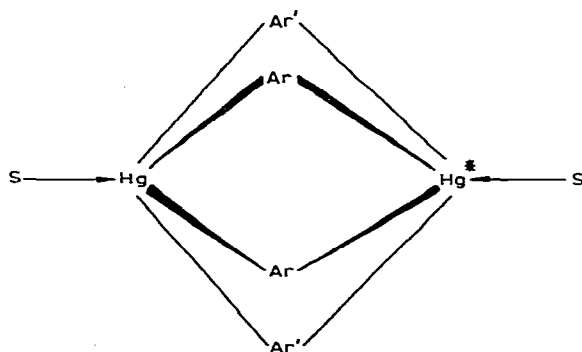
A polarographic technique recently employed by Reutov *et al.*⁶ to trace the exchange of organic radicals between diphenylmercury and a series of chemically active disubstituted mercury compounds is only applicable to reactions of type (a).

The preliminary examination of the exchange of radioactive mercury between diphenylmercury and bis(*p*-chlorophenyl)mercury in pyridine, was conducted under relatively forcing conditions. Separation of the reactants revealed that the exchange had achieved equilibrium without the formation of new reaction products [type (b)], which was in agreement with Reutov's initial observation⁷. The exchange was further shown to have attained equilibrium under the mildest conditions employed and the rate constant for the exchange could not be determined by the crystallisation method. Nor was the apparent rate of exchange reduced to a measurable level by conducting the reaction in a number of different solvents. Solvent dependent rate constants have been observed in a number of homogeneous¹⁵ and heterogeneous¹⁶ exchange reactions of organomercury compounds. This has been attributed to the formation of weakly bound solvent complexes with the organomercury compound, the greater the coordinating power of the solvent the stronger the binding. The latter reduces the electrophilic character of the metal atom and therefore the rate of reaction. In every case employed in the study the label was observed to be equilibrated between the reactants by the time the separation had been achieved.

Partition analysis yielded a rate constant of the order of $1 \times 10^{-7} \text{ mole} \cdot \text{l}^{-1}$ for the exchange between labelled diphenylmercury and bis(*p*-chlorophenyl)mercury. The individually determined rate constants exhibited considerable variation about a

mean value (Table 1) but within a given reaction series the temperature dependence of the rate constant permitted an evaluation of the activation parameters for the exchange (Table 1).

The reaction conditions employed, namely low temperature and an organic medium, ruled out the significant occurrence of ionic or radical initiated processes within the exchange reaction. Exchange via the commonly observed bimolecular mechanisms for electrophilic substitution (*i.e.* S_E2 and S_{Ei}) would lead to scrambling of the organic radicals in the product [type (a)]. In this case the unsymmetrical (*p*-chlorophenyl)phenylmercury was not detected indicating that the exchange occurred via a unique transition state. An octahedral distribution of species within the transition state would permit the simultaneous transfer of aryl radicals from one mercury atom to the other. Such a transition state is not inconsistent with the electronic structure, and it is interesting to note that a solvent effect with electron donating solvents would be expected, as one or two coordinated solvent molecules would distort the linear molecule and favour the formation of this transition state. This is further supported by the synthesis of unsymmetrical disubstituted organomercury compounds¹⁴, which would presumably exist in an equilibrium mixture of components if exchange with scrambling could occur:



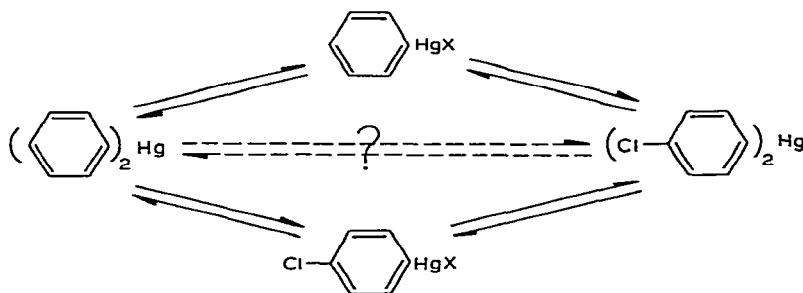
Transition state

The relatively large entropy of activation for this exchange conformed to the entropy values determined for similar reactions involving the simultaneous transfer of two organic radicals. Such a transition state has been considered to account for the exchange reaction between (*cis*-2-methylcyclohexyl)neophylmercury and mercuric iodide¹⁸ and between phenylethylmercury and mercuric chloride¹⁹. Jenson and Rickborn²⁵ recently proposed such a transition state for this particular reaction, but in no case has its presence been firmly established.

An examination of the exchange data revealed that to some extent the rate constant was dependent upon the mode of preparation of the reactants (*i.e.* series *c* and *d*, Table 1). Further, within a given series of determinations employing reactants from the same batch, the rate of exchange did not conform to a typical bimolecular rate relationship (Table 1). The coincidence of the $-\log(1-F)$ vs. time plots for this

series confirmed that the exchange was subject to some other influence (Fig. 1). Thin layer chromatography revealed the presence of small quantities of impurity within the system (Table 2). Although the character of these impurities was not fully established, they were identified as aryl mercuric salts from the R_f values. The presence of (*p*-chlorophenyl)mercuric halides was attributed to the method of synthesising the precursor, when these halides are the "half-reaction" products in the Grignard reaction sequence. It is also possible that the impurities contain small amounts of hydrolysis or oxidation products of the reactants. Only chromatography over thick layers of silica gel revealed the presence of impurities in the starting material and the reaction mixture. It is possible that additional hydrolysis took place during chromatography, though was still present to a kinetically significant extent during exchange.

To investigate the significance of the presence of these impurities a brief study was made of the so called "3-aryl" type exchange reactions. Employing the techniques described above the exchange of radioactive mercury between diphenylmercury and a selection of phenylmercuric salts of different electrophilic character was examined. Once again exchange was shown to be facile even under the mildest conditions. Thus the authenticity of the octahedral transition state for the 4-aryl exchange was not fully established because the label could be carried between diphenylmercury and bis(*p*-chlorophenyl)mercury by the small quantities of arylmercuric salts that are unavoidably present within the system. The presence of small amounts of radioactive mercury ($\leq 3\%$ of the total activity) within these impurities in the equilibrated 4-aryl system was taken as confirmation of the hypothesis, thus:



Work is continuing on this difficult but interesting reaction sequence.

REFERENCES

- 1 H. B. CHARMAN, E. D. HUGHES AND C. K. INGOLD, *J. Chem. Soc.*, (1959) 2523 *et seq.*
- 2 L. G. MAKAROVA AND A. N. NESMEYANOV, *The Organic Compounds of Mercury*, North Holland, 1967.
- 3 C. K. INGOLD, *Structure and Mechanism in Organic Chemistry*, G. Bell, 2nd ed., 1969.
- 4 H. B. CHARMAN, E. D. HUGHES, C. K. INGOLD AND H. C. VOLGER, *J. Chem. Soc.*, (1961) 1142.
- 5 M. D. RAUSCH AND J. R. VAN WAZER, *Inorg. Chem.*, 3 (1964) 761. R. E. DESSY, F. KAPLAN, G. R. COC AND R. M. SALINGER, *J. Amer. Chem. Soc.*, 85 (1963) 1191. G. R. REYNOLDS AND S. R. DANIEL, *Inorg. Chem.*, 6 (1967) 480.
- 6 I. P. BELETSKAYA, K. P. BUTIN, V. N. SHISHKIN AND O. A. REUTOV, *J. Organometal. Chem.*, 23 (1970) 31.
- 7 O. A. REUTOV, T. A. SMOLINA AND HU HUNG WENG, *Bull. Acad. Soc. USSR Div. Chem. Sci.*, (1959) 534.
- 8 O. A. REUTOV, *Rec. Chem. Prog.*, 22 (1959) 1.
- 9 (a) E. DREHER AND R. OTTO, *Chem. Zentr.*, 2 (1912) 822; (b) M. O. FORSTER, *J. Chem. Soc.*, 73 (1898) 783; (c) R. E. DESSY AND J. Y. KIM, *J. Amer. Chem. Soc.*, 82 (1960) 686.

- 10 (a) R. E. DESSY AND Y. K. LEE, *J. Amer. Chem. Soc.*, 82 (1961) 689; (b) FR. HEIN AND K. WAGLER, *Ber.*, 58 (1925) 1499.
 - 11 (a) M. A. KAZANKOVA, I. F. LUTSENKO AND A. N. NESMEYANOV, *Zh. Obshch. Khim.*, 35 (1965) 1447; (b) L. R. BARLOW AND T. M. DAVIDSON, *Chem. Ind. (London)*, (1965) 1956.
 - 12 A. N. NESMEYANOV AND D. N. KRAUSTOV, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1962) 431.
 - 13 D. R. POLLARD AND J. V. WESTWOOD, *J. Amer. Chem. Soc.*, 87 (1965) 2809; 88 (1966) 1404.
 - 14 (a) M. S. KHARASCH AND A. L. FLENNER, *J. Amer. Chem. Soc.*, 54 (1932) 674; (b) M. S. KHARASCH, H. PINS AND J. H. LEVINE, *J. Org. Chem.*, 3 (1938) 347; (c) H. GILMAN AND H. L. YALE, *J. Amer. Chem. Soc.*, 72 (1950) 8.
 - 15 K. P. BUTIN, A. N. RYATSTER, V. S. PETROVSAN, I. P. BELETSKAYA AND O. A. REUTOV, *Proc. Acad. Sci. USSR Div. Chem. Sci.*, 133 (1968) 1328.
 - 16 (a) R. A. G. MARSHALL AND D. R. POLLARD, *J. Amer. Chem. Soc.*, 92 (1970) 6723; (b) R. A. G. MARSHALL AND D. R. POLLARD, *J. Organometal. Chem.*, 25 (1970) 287.
 - 17 S. WINSTEIN, T. G. TRAYLOR AND C. GARNER, *J. Amer. Chem. Soc.*, 77 (1955) 3741.
 - 18 R. E. DESSY, Y. K. LEE AND J. Y. KIM, *J. Amer. Chem. Soc.*, 83 (1961) 1163.
 - 19 F. R. JENSEN AND B. RICKBORN, *Electrophilic Substitution of Organomercurials*, McGraw-Hill, 1968.
- J. Organometal. Chem.*, 36 (1972)