14. *Molar Refraction in Some Organic Compounds of Mercury.*

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Molar refractions, computed from measurements of $n_D^{15°}$ on organic mercurials, indicate that, in the series HgR_2 and $HgRCl$, contributions of Hg are 11·0 and 11·4 and of CH_2 4·90 and 4·76, respectively. The abnormally high values for CH_2, compared with the mean literature value of 4·64, are attributed to a " loosening " of electrons owing to the proximity of the negatively-charged electron shells of the mercury atom. Similar effects are encountered with aromatic and olefinic derivatives of mercury. In the series $HgRCl$ chain-branching produces optical exaltation. By consideration of the series HgR_2 and $HgRCl$, values for the Cl octet and for the C–Hg covalent bond are larger than those encountered in similar molecules when mercury atoms are absent. The ascertained value for the Cl octet progressively diminishes as R increases. An interpretation based on electronic configuration is advanced.

VALUES of $[R]_D$ (Tables I—III) have been ascertained for organic mercurials—(a) mercury dialkyls HgR_2 (R up to octyl), (b) alkylmercury chlorides $HgRCl$ (R up to octyl), (c) aromatic derivatives, and (d) olefinic derivatives—in order to establish (i) the contributions of Hg and CH_2 in the series HgR_2 and $HgRCl$; (ii) the influence of temperature on $[R]_D$ values in the series HgR_2; (iii) the effects arising from chain-branching in $HgRCl$; (iv) the possible existence of optical anomalies in aromatic and olefinic derivatives of mercury.

The members of the series HgR_2 were liquid and were measured directly. The solid substances, comprising the other series of mercurials, were measured in solution in suitable solvents. Table IV contains relevant data on solvents and on substances used for comparison. The values showed under $[R]$,calc. in Tables III and IV are derived from Eisenlohr's values (*Z. physikal. Chem.*, 1910, **75**, 585) for all except Hg, for which the value of 11·2 (derived from results for the series HgR_2 and $HgRCl$) has been employed (see below).

(1) *Atomic constant for mercury.* In the series HgR_2, on plotting $[R]_D^{15°}$ against the number of CH_2 groups (n), the extrapolated value of $[R]$ when $n = 0$ represents the constants for (Hg + 2H) and is 13·2 ± 0·1. Eisenlohr's value of H = 1·10 being assumed (cf. Vogel's value of H = 1·028; *J.*, 1946, 134), the constant for mercury is 11·0 ± 0·1. Similarly in the series $HgRCl$, the extrapolated value when $n = 0$ represents (Hg + H + Cl) and is 18·5 ± 0·1. Eisenlohr's values of H = 1·10 and Cl = 5·97 being assumed, the constant for mercury is 11·4 ± 0·1. The mean constant for mercury from the two series is 11·2 and will be used in subsequent calculations. It is supported by refraction measurements of mercuric chloride in *cyclo*hexanone (Table IV) : the calculated value of $[R]$ based on Hg = 11·2 agrees well with the observed value.

(2) *Constant for* CH_2. The refraction constants for CH_2 in the series HgR_2 and $HgRCl$ are represented by the slopes of the respective linear graphs referred to in (1), the respective values being 4·90 ± 0·02 and 4·76 ± 0·02. Eisenlohr obtained the mean value of 4·618, and Vogel

TABLE I.

Molar refractions in the series HgR₂. *

R.	$[R]_D^{15°}$.	$[R]_D^{20°}$.	Increase % per ° c.	R.	$[R]_D^{15°}$.	$[R]_D^{20°}$.	Increase % per ° c.
Me	22·874	22·890	0·014	Bu^i	52·042	52·110	0·026
Et	32·743	32·769	0·016	Am^n	62·231	62·281	0·016
Pr^n	42·456	42·468	0·006	n-C$_8$H$_{17}$	91·572	91·604	0·007
Bu^n	52·084	52·116	0·012				

* Values ± 0·01.

TABLE II.

Molar refractions, $[R]_D^{15°}$, in the series HgRCl. *

	Solvent.						
		cyclo-					Diff. from
R.	Pyridine.	Hexanone.	Westron.	R.		Pyridine.	n-compound.
Me	23·39	23·3	23·5	Pr^i		32·78	−0·13
Et	28·13	28·3	28·3	Bu^i		37·40	−0·12
Pr^n	32·91	32·9	32·9	Bu^s		37·97	+0·45
Bu^n	37·52	37·3	37·7	Bu^t		38·06	+0·54
Am^n	42·35	42·4	42·6	Am^i		42·30	−0·05
n-C$_8$H$_{17}$	56·60	—	—	CHMePr^i		42·35	nil

* ± 0·05 in pyridine; ± 0·2 in *cyclo*hexanone and in Westron.

TABLE III.

Molar refractions of olefinic and aromatic derivatives of mercury.

Compound.	$[R]_D^{15°}$.*	$[R]$, calc.	Optical anomaly.	Compound.	$[R]_D^{15°}$.*	$[R]$, calc.	Optical anomaly.
			In *cyclo*hexanone.				
Hg(CCl:CHCl)₂ ...	51·0	50·4	+0·6	Hg(CCl:CCl₂)₂ ...	62·1	60·1	+2·0
HgCl(CCl:CHCl)...	37·4	36·8	+0·6				
			In pyridine.				
HgPh₂	64·7	61·6	+3·1	HgCl·C₆H₄Me (p)	49·3	47·0	+2·3
HgPhCl	43·7	42·4	+1·3	HgCl·C₁₀H₇ (α) ...	61·6	57·7	+3·9
HgCl·C₆H₄Me (o)	49·5	47·0	+2·5	,, (β) ...	62·6	57·7	+4·9
,, (m)	49·7	47·0	+2·7				

* ± 0·1.

TABLE IV.

Molar refractions of other compounds.

Compound.	$[R]_D^{15°}$.	Accuracy.	$[R]$, calc.	Optical anomaly.	Compound.	$[R]_D^{15°}$.	Accuracy.	$[R]$, calc.	Optical anomaly.
C₆H₆	26·16	±0·01	26·31	−0·15	C₁₀H₈	44·06	±0·05	41·6	+2·4
C₆H₅Cl	31·15	±0·01	31·17	−0·02	C₆H₅·C₆H₅	52·43	±0·05	50·42	+2·0
C₆H₅Me	31·08	±0·01	30·93	+0·15	HgCl₂	23·04	±0·05	23·1	+0·06

4·647 (*loc. cit.*) from various homologous series of organic compounds. It is concluded that the presence of mercury in organic compounds causes a definite increase in the CH₂ constant. The electronic significance of this fact is discussed below.

This new method of approach to the problem, therefore, yields a result of great significance in discussing the problem from the standpoint of electronic configuration. By assuming that the Eisenlohr value for CH₂ could be utilised for the first six *normal* members of the series. HgR₂, Jones, Evans, Gulwell, and Griffiths (*J.*, 1935, 39) concluded that the constant for Hg varied between 12·28 and 13·43. But this conclusion would appear to be invalidated by the reported constancy of the Hg contribution (see above).

(3) *Variation of $[R]_D$ with temperature in the series* HgR₂. The rate of increase of $[R]_D$ with temperature (Table I) varies between 0·006 and 0·026% per degree, in good agreement with the observation that liquids generally show values between 0·005 and 0·015.

(4) *The effects of branching in the alkyl chain in the series* HgRCl. From the few isomers examined (Table II), it would appear that *iso*-compounds give good agreement with n-compounds.

whilst *sec.*- and *tert.*-isomers may show exaltations of the order of 0·5 c.c. These results agree with the general results obtained by Vogel (*J.*, 1943, 636) using a wide range of isomeric alkyl halides. The exaltations are not as large as those observed in branched-chain members of the series HgR_2, SnR_4, and PbR_4 (Jones *et al., loc. cit.*), since only one alkyl chain exists in the molecule.

(5) *Optical anomalies in olefinic and aromatic derivatives of mercury.* The three olefinic derivatives of mercury (Table III) show respective optical exaltations of 0·6, 0·6, and 2·0 c.c. Since chlorine-substituted olefins do not normally show large optical anomalies, these observed exaltations are attributed to the presence of the mercury atom. Diphenylmercury shows an optical exaltation of 3·1 c.c. which is attributed to the presence of the mercury atom because (*a*) phenyl behaves normally (cf. benzene, chlorobenzene, toluene) and (*b*) the exaltation cannot be analogous to that occurring in diphenyl because the latter exaltation is due to conjugation passing from one ring to the other, an effect which is prevented in diphenyl mercury by the interposed mercury atom. Phenylmercury chloride and the three tolylmercury chlorides similarly show optical exaltations which must be due to the presence of mercury, since no large optical exaltations occur in chlorobenzene and toluene. The α- and β-naphthylmercury chlorides show optical exaltations of 3·9 and 4·9 c.c., respectively, compared with 2·4 c.c. in naphthalene itself. These increases of 1·5 and 2·5, respectively, are attributed to the presence of mercury.

(6) *Electronic aspects.* The electronic interpretation of refraction of light has been developed by Smyth (*Phil. Mag.*, 1925, **50**, 361) and Fajans (*Ber.*, 1926, **59**, 249) and the relevant octet and bond constants have been calculated. The latter author (" Physical Methods of Organic Chemistry ", Vol. I, edited by Weissberger) puts forward the following conclusions :— (*a*) Molar refraction measures the electronic polarisability of the molecule, [*R*] increasing as the electrons become more loose; (*b*) an electronic system is tightened by adjacent positive charges and loosened by adjacent negative charges; (*c*) when, within a given electronic system the nuclear charge is split, or the distribution of positive charges becomes less symmetrical, the electronic system is loosened (this explains the differences observed in the molar refractions of isomers); (*d*) the observed increase of molar refractions with increasing temperature is a real indication of the loosening of the electronic shell due to the increase of distance between the molecules. This effect has already been measured and discussed for the series HgR_2 (Table I).

The constant for the Cl′ octet in HgRCl is given by $(HgRCl - \frac{1}{2}HgR_2)$. From the figures shown in Tables I and II, the following values are obtained :

R =	Me.	Et.	Pr^n.	Bu^n.	Bu^i.	Am^n.	n-C_8H_{17}.
Cl′ octet	11·95	11·76	11·68	11·48	11·38	11·23	10·82

Comparing these with the value of 9·07 for the detached Cl′ ion (Fajans and Joos, *Z. Physik*, 1924, **23**, 1), it is concluded that the chlorine octet is influenced by a neighbouring negative charge which loosens the system, and that the influence decreases as the chain length increases. It is suggested that the loosening effect is caused by the large number of orbital electrons of the mercury atom which screen the effect of the comparatively remote positively-charged nucleus.

Meanwhile, the only other recipient of this negative-charge effect is the alkyl chain on the other side of the Hg nucleus. As the chain becomes longer it will absorb a larger share of the influence, and the refraction value of the Cl′ octet decreases steadily until presumably it reaches a limiting value.

The following data support this idea : (i) the refraction constant for the Cl′ octet in mercuric chloride is given by $\frac{1}{2}HgCl_2$ and equals 11·52. This value agrees well with the values in the series HgRCl, and proves that the high values in the latter series cannot be due to the presence of the alkyl chain; (ii) the abnormally high CH_2 values found in the series HgR_2 and HgRCl also indicate the proximity of a negative charge; (iii) Vogel (*J.*, 1943, 638) examined numerous alkyl chlorides, bromides, and iodides, and obtained the respective mean CH_2 refraction values 4·641, 4·646, and 4·656. As we pass from RCl ⟶ RBr ⟶ RI successive shells of orbital electrons are added to the halogen atom, with corresponding increases in electronic looseness. On comparing the larger electron shells of mercury with those of bromine and iodine, the correspondingly larger loosening effect is readily appreciated; (iv) the number and configuration of orbital electrons in lead closely resemble those of mercury. The molar refractions of the first few members of the series PbR_4 (Jones *et al., loc. cit.*) yield CH_2 values by difference which are also abnormally high.

The refraction value of the C:Hg *covalent bond.* In the dialkylmercury series this value is equal to $[\frac{1}{2}HgR_2 - 3(C:H) - (n - 1)CH_2]$, where n has the usual significance. Now

$C^{..}H = \frac{1}{4}CH_4 = (\frac{1}{4}C + H) = 1.70$ with Eisehlohr's constants, and $CH_2 = 4.90$ in this series. Hence we obtain the following $C^{..}Hg$ bond values :

R =	Me.	Et.	Pr^n.	Bu^n.	Am^n.	n-C_8H_{17}.
Bond value	6·33	6·37	6·33	6·24	6·42	6·38

The mean value is 6.3 ± 0.1 and does not vary with chain length. Comparing this with the C–C single-bond value of 1·21, it is concluded that the two electrons in the C–Hg bond are extremely loose. This fact also points to the presence of a neighbouring negative influence and is satisfactorily explained by the " screening " effect mentioned above.

The olefinic and aromatic derivatives. These compounds (Table III) may also be considered electronically.

(*a*) In 1 : 2-dichlorovinylmercury chloride (*s*-dichloroethylene mercurichloride) the refraction constant of the Cl′ octet is given by $(37.4 - \frac{1}{2} \times 51.0) = 11.9$, in good agreement with the corresponding constants in the series HgRCl.

(*b*) An estimation of the C–Hg bond value in bis-1 : 2-dichlorovinylmercury (mercury bis-*s*-dichloroethylene) can be made on the assumption that the other links have their normal values :

$$C^{..}Hg = \frac{1}{2} \times 51.0 - 2 \text{ Cl′ octets} - (C^{..}H) - (C^{..}C)$$
$$= 25.5 - (2 \times 6.57) - 1.70 - 4.15 = 6.5$$

which agrees well with the mean value for the series HgR$_2$ (above).

(*c*) In bistrichlorovinylmercury (mercury bistrichloroethylene), the $C^{..}Hg$ bond constant is given by

$$\frac{1}{2} \times 62.1 - 3 \text{ Cl′ octets} - (C^{..}C)$$
$$= 31.05 - (3 \times 6.57) - 4.15 = 6.2$$

which agrees well with the mean value for the series HgR$_2$.

(*d*) The Cl′ octet constant in phenylmercury chloride is given by HgPhCl $- \frac{1}{2}$(HgPh$_2$) and equals 11·35, which agrees well with corresponding values in the series HgRCl.

EXPERIMENTAL.

Physical Measurements.—Refractive indices of the purified liquids and solutions were measured with a Bellingham and Stanley Abbé refractometer reading to 0·0001 at a temperature controlled to within $\pm 0.1°$. Illumination was from a sodium lamp. With pure liquids, readings were taken at various temperatures between 10° and 25° from which $n^{15°}$, $n^{20°}$, and dn/dθ were evaluated.

When examining solutions, the prisms were maintained at 15·0° continuously. After 3 minutes, three successive readings were made at 2-minute intervals. The fact that the 3 readings were identical proved that the solution was at constant temperature, and that the solvent was not evaporating appreciably. A special entrance duct made it unnecessary to open out the prisms when charging them with solution, and charging was effected very rapidly by means of a glass tube. As a further check, after one set of observations had been taken, the prisms were opened, cleaned, dried, closed, and charged with another portion of the solution; a reading was taken after 3 minutes in order to check the previous 3 readings.

Densities were measured by a glass pyknometer, capacity approximately 5 c.c., calibrated with redistilled water and pure benzene.

Mercury Dialkyls.—Dimethylmercury. 15 Lb. of 0·40% sodium amalgam were placed in a 2-l. aspirator bottle which was placed with its axis horizontal in a sink. The opening at the top of the bottle was securely stoppered with a rubber bung and the side opening was fitted with a reflux condenser. 80 G. of methyl iodide and 10 g. of ethyl acetate were added down the condenser. The reaction took place briskly, and the bottle was initially kept cool with a stream of running water. After 12 hours the

TABLE V.

Compound.	M. p.	Compound.	M. p.	Compound.	M. p.
HgMeCl	175°	HgPh$_2$	122°	Hg(CCl:CHCl)$_2$	50·3°
HgEtCl	195	HgPhCl	255	HgCl(CCl:CHCl)	85·6
HgPr^{n}Cl	144	HgCl·C$_6$H$_4$Me (*o*)	146	Hg(CCl:CCl$_2$)$_2$	141
HgPr^{i}Cl	94·2	,, (*m*)	163		
HgBu^{n}Cl	129	,, (*p*)	234		
HgBu^{i}Cl	49·0	HgCl·C$_{10}$H$_7$ (*α*)	183		
HgBu^{s}Cl	—	,, (*β*)	271		
HgBu^{t}Cl	(decomp.)				
HgAm^{n}Cl	124				
HgAm^{i}Cl	93·2				
HgCl·CHMePr^i	—				
HgCl·C$_8$H$_{17}$	115				

TABLE VI.

R.	W_2.	W_1.	n.	ρ.	M_2.	$[R]_2$.
			Solvent : pyridine.			
Me	3·6828	9·2476	1·5281	1·2618	251·09	23·39
Et	2·0387	11·3162	1·5201	1·1100	265·11	28·13
Pr^n	2·4296	8·4859	1·5223	1·1616	279·13	32·91
Bu^n	2·6248	9·4850	1·5209	1·1445	293·15	37·52
Am^n	1·1721	6·7909	1·5172	1·0821	307·17	42·35
n-C$_8$H$_{17}$	1·2493	9·5260	1·5142	1·0468	349·29	56·65
,,	0·8463	9·3652	1·5133	1·0286	349·29	56·54
Pr^i	1·1582	7·5390	1·5188	1·0864	279·13	32·78
Bu^i	2·0358	7·7867	1·5198	1·1358	293·15	37·40
Bu^s	3·2586	10·0133	1·5236	1·1703	293·15	37·97
Bu^t	1·0930	9·0166	1·5171	1·0605	293·15	38·06
Am^i	1·3645	9·4871	1·5161	1·0666	307·17	42·30
CHMePr^i	0·8965	8·1131	1·5163	1·0507	307·17	42·35
			Solvent : *cyclo*hexanone.			
Me	1·6594	20·067	1·4575	1·0064	251·09	23·31
Et	0·8521	42·644	1·4550	0·96174	265·11	28·31
Pr^n	1·1354	13·759	1·4577	0·99955	279·13	32·91
Bu^n	0·9033	38·422	1·4550	0·96290	293·15	37·32
Am^n	0·5953	20·805	1·4559	0·96554	307·17	42·36
			Solvent : Westron.			
Me	1·1089	28·751	1·5004	1·6439	251·09	23·46
Et	0·6168	28·791	1·4991	1·6249	265·11	28·28
Pr^n	1·2076	34·490	1·4996	1·6313	279·13	32·89
Bu^n	0·9987	38·035	1·4990	1·6226	293·15	37·68
Am^n	0·8844	35·932	1·4988	1·6190	307·17	42·58

Solute.	W_2.	W_1.	n.	ρ.	M_2.	$[R]_2$.
Hg(CCl:CHCl)$_2$	3·0787	8·6591	1·4742	1·1488	392·45	50·94
	1·4051	6·9326	1·4662	1·0680	392·45	51·05
HgCl(CCl:CHCl)	1·3491	8·7002	1·4637	1·0510	331·99	37·43
	0·5859	8·8505	1·4583	0·9934	331·99	37·34
Hg(CCl:CCl$_2$)$_2$	2·5898	8·8085	1·4728	1·1160	461·35	62·08
	1·1390	6·7431	1·4654	1·0486	461·35	62·22
HgPh$_2$	3·1749	13·3344	1·5317	1·1037	354·17	64·53
	3·2733	10·1444	1·5374	1·1386	354·17	64·70
	2·7464	8·8219	1·5366	1·1347	354·17	64·78
HgPhCl	1·8175	8·8025	1·5282	1·1160	313·11	43·72
HgCl·C$_6$H$_4$Me (o)	2·2661	8·1115	1·5318	1·1463	327·13	49·66
	0·5371	6·5816	1·5191	1·0375	327·13	49·40
,, (m)	0·8299	9·6754	1·5192	1·0393	327·13	49·66
	0·5650	8·6904	1·5172	1·0263	327·13	49·73
,, (p)	1·6165	8·3328	1·5263	1·0997	327·13	49·36
	0·9482	7·2641	1·5224	1·0656	327·13	49·23
HgCl·C$_{10}$H$_7$(a)	1·3110	8·0050	1·5298	1·0825	363·13	61·72
	0·4133	7·7395	1·5183	1·0198	363·13	61·59
,, (β)	0·7667	10·0735	1·5209	1·0325	363·13	62·61
	0·1020	7·7065	1·5140	0·99542	363·13	62·65

Solute.	Solvent.	W_2.	W_1.	n.	ρ.	M_2.	$[R]_2$.
C$_{10}$H$_8$	*cyclo*Hexanone	2·3421	9·6722	1·4851	0·96458	128·06	44·16
	Westron	2·0723	14·5983	1·5198	1·5019	128·06	43·96
	,,	1·3437	14·8942	1·5128	1·5356	128·06	43·95
	Toluene	1·4553	10·5086	1·5124	0·88702	128·06	44·18
Ph·Ph	*cyclo*Hexanone	2·1532	12·3248	1·4763	0·96036	154·08	52·56
	Pyridine	2·2690	9·3005	1·5323	0·99630	154·08	52·38
	Quinoline	1·8828	8·8170	1·6280	1·0863	154·08	52·36
HgCl$_2$	*cyclo*Hexanone	4·8352	12·2459	1·4779	1·2366	271·52	23·11
	,,	6·6467	15·0182	1·4801	1·2688	271·52	22·98

Liquid.	$n^{15°}$.	$\rho^{15°}$.	M.	$[R]$.	Liquid.	$n^{15°}$.	$\rho^{15°}$.	M.	$[R]$.
Benzene	1·5044	0·88400	78·05	26·16	Pyridine	1·5121	0·98670	79·05	24·04
Chlorobenzene	1·5275	1·1112	112·50	31·15	Quinoline	1·6287	1·0967	129·06	41·80
Westron	1·4977	1·6066	167·84	30·60	Toluene	1·4988	0·86940	92·06	31·08
*cyclo*Hexanone	1·4541	0·94840	98·08	28·76					

reaction was complete, and the whole mass was white and solid, owing to formation of sodium iodide. The mercury was poured off, and the residue shaken with a large volume of water and separated. The lower layer was shaken repeatedly with water, 2N-sodium hydroxide, and then water until clean. After standing overnight over anhydrous sodium sulphate the liquid was distilled under reduced pressure. The middle fraction was collected and refractionated to constant refractive index; yield (crude), 45 g. (65%); b. p. 92°; $n^{15°}$ 1·5480, $n^{20°}$ 1·5452, $dn/d\theta = -0·00057$; $\rho^{15°}$ 3·2029, $\rho^{20°}$ 3·1874, $d\rho/d\theta = -0·0031$.

Diethylmercury. This was similarly prepared from 15 lb. of 0·39% sodium amalgam, 300 g. of ethyl iodide, and 40 g. of ethyl acetate. The reaction was complete after 24 hours; yield (crude) 168 g. (67%); b. p. 69°/26 mm.; $n^{15°}$ 1·5513, $n^{20°}$ 1·5487, $dn/d\theta = -0·00053$; $\rho^{15°}$ 2·5221, $\rho^{20°}$ 2·5107, $d\rho/d\theta = -0·0023$.

Di-n-butylmercury. With 16 lb. of 0·40% sodium amalgam, 112 g. of n-butyl iodide, and 24 g. of ethyl acetate, reaction was complete after 3 days; yield (crude) 61 g. (64%); b. p. 105°/7 mm.; $n^{15°}$ 1·5104, $n^{20°}$ 1·5081, $dn/d\theta = -0·00047$; $\rho^{15°}$ 1·8090, $\rho^{20°}$ 1·8010, $d\rho/d\theta = -0·0016$.

Diisobutylmercury. Similarly prepared, this had b. p. 82°/10 mm.; $n^{1 ·°}$ 1·4988, $n^{20°}$ 1·4966, $dn/d\theta = -0·00045$; $\rho^{15°}$ 1·7755, $\rho^{20°}$ 1·7666, $d\rho/d\theta = -0·0018$.

Di-n-amylmercury. This compound had b. p. 157°/19 mm.; $n^{15°}$ 1·5006, $n^{20°}$ 1·4986, $dn/d\theta = -0·00042$; $\rho^{15°}$ 1·6221, $\rho^{20°}$ 1·6153, $d\rho/d\theta = -0·0014$.

Di-n-propylmercury. To the Grignard reagent prepared from n-propyl chloride (67 g.), magnesium (20 g.), and ether (750 c.c.) was added dry mercuric chloride (116 g.). The mixture was stirred with water, separated, and dried (Na_2SO_4). The ether was distilled off, and the product fractionated under reduced pressure to constant refractive index; yield before fractionation, 80 g. (65%); b. p. 106—110°/11 mm.; $n^{15°}$ 1·5213, $n^{20°}$ 1·5190, $dn/d\theta = -0·00048$; $\rho^{15°}$ 2·0578, $\rho^{20°}$ 2·0484, $d\rho/d\theta = -0·0019$.

Di-n-octylmercury. The preparation was analogous to the preceding one. As the product could not be distilled, it was purified by removal of impurities by heating to 110°/4 mm. on a brine bath to constant refractive index; $n^{15°}$ 1·4900, $n^{20°}$ 1·4880, $dn/d\theta = -0·00040$; $\rho^{15°}$ 1·3483, $\rho^{20°}$ 1·3431, $d\rho/d\theta = -0·00010$.

Alkyl Mercurichlorides.—To a solution of the dialkylmercury in cold ethanol, a solution of the calculated amount of mercuric chloride in cold ethanol was added. After a few seconds, the product separated as a white crystalline precipitate, which was filtered off, washed with cold ethanol, and recrystallised from hot ethanol to constant m. p. The crystals were dried by air current at the pump. The corrected m. p.s are given in Table V.

Aromatic and Olefinic Derivatives.—These were all supplied in a highly purified condition by Mr. M. FitzGibbon of Messrs. Lunevale Products, Ltd., Lancaster. Corrected m. p.s are shown in Table V. The three olefinic derivatives have been described by FitzGibbon (*J.*, 1938, 1218).

On refluxing mercuric acetate, benzene, and glacial acetic acid for a few hours, phenylmercury acetate is formed which, on the addition of concentrated aqueous sodium chloride, precipitates the chloride. The latter reacts with thiourea to give diphenylmercury.

The compounds HgXCl (X = o-, m-, and p-tolyl, and α- and β-naphthyl) were prepared from X·NH₂ by diazotisation and addition of mercuric chloride, forming X·N₂Cl,HgCl₂, which reacts with copper powder in ethanol, yielding HgXCl, nitrogen, and cuprous chloride.

The solvents were purified by fractional distillation to constant refractive index. Naphthalene was purified by sublimation to constant m. p. (80°), and diphenyl was recrystallised from ethanol to constant m. p. (70·5°). Mercuric chloride was purified by repeated sublimation.

Calculation of Molar Refractions of Solids in Solution.—The molar refraction of the solution is measured and the contribution of the solvent is subtracted from it. Then it may be shown that

$$[R]_2 = \frac{M_2}{W_2} \left[\frac{n^2 - 1}{n^2 + 2} \cdot \frac{W_1 + W_2}{\rho} - \frac{n_1^2 - 1}{n_1^2 + 2} \cdot \frac{W_1}{\rho_1} \right]$$

where n and ρ refer to the solution, n_1, ρ_1, and W_1 to the solvent, and $[R]_2$, m_2, and W_2 to the solute (W = mass of substance used; M = molecular weight). This reasoning assumes that the molar contributions of solute and solvent are strictly additive, but it has been shown by Smyth, Engel, and Wilson (*J. Amer. Chem. Soc.*, 1929, **51**, 1736) that this assumption is correct for molecules which do not exert strong forces on each other, and deviations are not usually more than a few hundredths of a unit.

It was found necessary in this investigation to choose each solvent in conformity with the following limitations : (i) The volatility must not be too great at room temperature. (ii) It must not react with or allow ionisation of the solute. (iii) It must not be strongly polar. (iv) It must dissolve the solute appreciably; the above expression is of the type $[R]_2 = X (y - z)$, and as the solution is diluted, $(y - z)$ becomes smaller and x becomes larger, so that any error in y and/or z causes continuously larger proportional errors in the value of $[R]_2$.

The following solvents were used : pyridine, *cyclo*hexanone, Westron, toluene, and quinoline.

Individual experimental readings are given in Table VI. The accuracies of the results stated in Tables I—IV have been estimated assuming a maximum error of ±0·0001 in the reading of n.