722. *Aromatic Reactivity. Part XVII.*[1] *Cleavage of Aryltricyclohexylplumbanes by Aqueous-ethanolic Perchloric Acid.*

By C. Eaborn and K. C. Pande.

We have measured spectrophotometrically the rates of cleavage of some tricyclohexylphenylplumbanes, $X{\cdot}C_6H_4{\cdot}Pb(C_6H_{11})_3$ (where X = H, *p*-Me, *p*-OMe, *p*-Cl, and *m*-Cl), in aqueous-ethanolic perchloric acid.

The influences of substituents are consistent with the reaction's being regarded as an electrophilic aromatic substitution in which only a small demand is made on electromeric effects.

We have measured spectrophotometrically the rates of cleavage at 25·0° of some tricyclohexylphenylplumbanes in a mixture of ethanol (10 vol.) and aqueous perchloric acid (1 vol.). (We chose tricyclohexyl-lead derivatives for study because they are solids, and thus could be purified by recrystallization: organolead compounds tend to decompose on distillation.) The overall course of the reaction, which is an electrophilic aromatic substitution (aromatic protodetricyclohexylplumbylation), may be represented as:

$$X{\cdot}C_6H_4{\cdot}Pb(C_6H_{11})_3 + MOH \xrightarrow{H^+} X{\cdot}C_6H_5 + (C_6H_{11})_3Pb{\cdot}OM$$

$$(C_6H_{11})_3Pb{\cdot}OM + HClO_4 \rightleftharpoons (C_6H_{11})_3PbClO_4 + MOH$$

$$(M = H \text{ or } Et)$$

Table 1. *Cleavage of* $X{\cdot}C_6H_4{\cdot}Pb(C_6H_{11})_3$ *by aqueous-ethanolic perchloric acid at* 25·0°.

X	$[HClO_4]$[a] (M)	10^3k (min.$^{-1}$)	k_{rel}	X	$[HClO_4]$[a] (M)	10^3k (min.$^{-1}$)	k_{rel}
p-OMe	0·0022	53	21	H	0·053	63·6	1
p-Me	0·01	39·5	—	*p*-Cl	0·053	20·3	0·32
	0·022	88·1	3·4		0·097	36·8	—
H	0·01	11·8	1	*m*-Cl	0·097	14·4	0·125
	0·022	25·6	1				

[a] Concn. of aqueous acid, 1 vol. of which was added to 10 vol. of an ethanolic solution of the organoplumbane.

---

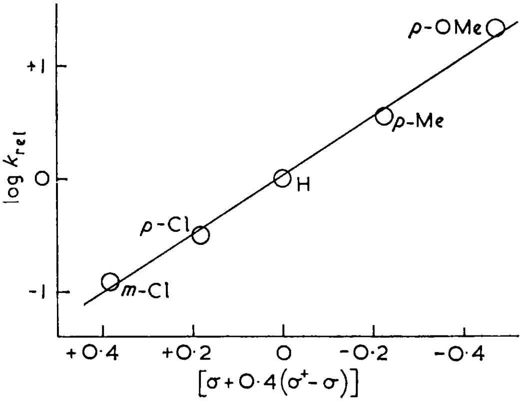
[1] Part XVI, Eaborn and Taylor, *J.*, 1961, 2388.

The results are shown in Table 1 as first-order rate constants, k, at the particular (added-)acid concentrations involved, along with values, k_{rel}, of rates relative to those of tricyclohexylphenylplumbane. The main features are as follows:

(i) At the low concentrations of acid used, the rate is proportional to the concentration of acid. (Use is made of this in deriving the value of k_{rel} for the *p*-methoxy-compound.) No doubt, at higher concentrations of acid, rates would rise more steeply than the acid concentration, as in analogous cleavages of aryl–Si, aryl–Ge, and aryl–Sn bonds.[2-4]

(ii) The spread of rates is smaller than in protodestannylation of aryltricyclohexylstannanes (in which k_{rel} for the *p*-methoxy-group, f_p^{OMe}, is 64 and for the *m*-chloro-group, f_m^{Cl}, is 0·039)[4] and much smaller than in protodegermylation of aryltriethylgermanes ($f_p^{\text{OMe}} = 540$; $f_m^{\text{Cl}} = 0{\cdot}0165$)[3] and protodesilylation of aryltrimethylsilanes ($f_p^{\text{OMe}} = 1500$; $f_m^{\text{Cl}} = 0{\cdot}008$).[2] This effect is associated with the greater reactivity of the lead compounds, which means that less reorganization of structure takes place between the initial state and the transition state, with less disturbance of the electrons of the aromatic ring.

(iii) A plot of log $k_{\text{rel}}^{\text{Pb}}$ against log $k_{\text{rel}}^{\text{Sn}}$ (the superscript denotes which protodemetalation is involved) is a good straight line. It follows that plots of log $k_{\text{rel}}^{\text{Pb}}$ against log $k_{\text{rel}}^{\text{Ge}}$ are not linear, since a linear free-energy relation exists between substituent effects in the desilylation and degermylation,[3] but not between those in these reactions and in protodestannylation.[4]



Effect of aryl-substitution on the rate of cleavage of tricyclohexylphenylplumbanes.

(iv) As in protodestannylation,[4] values of log k_{rel} in the deplumbylation are not linearly related to either σ or σ^+ constants,[5] but (see Figure) the relation[6] log $k_{\text{rel}} = \rho[\sigma + r(\sigma^+ - \sigma)]$, where $r = 0{\cdot}4$, applies ($\rho = 2{\cdot}5$) as in protodestannylation ($\rho = 3{\cdot}8$).[4] (Actually for the deplumbylation a value of $r = 0{\cdot}5$ gives a slightly better fit, but this is true also of the destannylation if attention is confined to the same substituents.) The small value of r indicates that the $+E$ effects of substituents operate less effectively than in most other electrophilic aromatic substitutions.[6]

"Electronegativity," and Ease of Cleavage of Aryl–Metal Bonds.—The relative ease of acid cleavage of organic groups from metals, particularly from mercury,[7] but also from lead,[8] has often been used as an indication of the relative electronegativities of the groups,

---

[2] Eaborn, *J.*, 1953, 3148; 1956, 4858.

[3] Eaborn and Pande, *J.*, 1961, 297.

[4] Eaborn and Waters, *J.*, 1961, 542.

[5] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[6] Yukawa and Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

[7] Kharasch and Flexner, *J. Amer. Chem. Soc.*, 1932, **54**, 674; Kharasch, Pines, and Levine, *J. Org. Chem.*, 1938, **3**, 347; Kharasch, Reinmuth, and Mayo, *J. Chem. Educ.*, 1934, **11**, 82.

[8] Gilman, Towne, and Jones, *J. Amer. Chem. Soc.*, 1933, **55**, 4689; Gilman and Towne, *Rec. Trav. chim.*, 1932, **51**, 1054; Leeper, Summers, and Gilman, *Chem. Rev.*, 1954, **54**, 101.

it being argued, in effect, that the group which most easily leaves with the electrons of the C–Metal bond (and combines with a proton of the acid) must be the more electronegative.[7-9] We have shown clearly in this series of papers that the ease of cleavage of aryl groups from silicon, tin, germanium, and lead by acid or halogen can be quantitatively explained in terms of the ease of electrophilic attack at the carbon of the aryl–metal bond, and that effects of substituents in the aryl group can be satisfactorily related to substituent effects in common electrophilic aromatic substitutions.[2-4,10,11]

It is likely that the ease of cleavage of covalent bonds between organic groups, including alkyl groups, and metals, including mercury (cf. ref. 12), is in general mainly determined by the ease of electrophilic attack at the carbon atom of the bond, and it should be abandoned as a measure of electronegativity of the groups (cf. refs. 13, 14).

EXPERIMENTAL

Aryltricyclohexylplumbanes.—These were prepared more easily than corresponding germanes [3,11,15] and, particularly, silanes,[11] no doubt because of the smaller steric effect of the cyclohexyl groups when attached to the larger metal atom.

Except where noted below, a solution of bromotricyclohexylplumbane (0·015 mole) in benzene (150 ml.) was added to a solution of aryl-lithium prepared from the appropriate aryl bromide (0·05 mole) and lithium (0·11 g.-atom) in ether (60 ml.), and the mixture was boiled under reflux for 1 hr. An excess of water was added, with the usual precautions, and the organic layer was separated, washed, and dried (Na_2SO_4). The solvent was removed and the residue was recrystallized from ethanol, to give the *aryltricyclohexylplumbanes* in fine white crystals.

In the case of the *p*-chloro-compound the aryl-lithium was prepared from *p*-bromochlorobenzene (0·05 mole) and n-butyl-lithium (0·05 mole) in ether (50 ml.). In the case of the *p*-dimethylamino-compound the reflux period was replaced by 1 hr. at room temperature.

In the case of the *m*-chloro-compound, the *m*-chlorophenyl-lithium was prepared from *m*-chlorobromobenzene (0·042 mole) and n-butyl-lithium (0·04 mole) at −30°, bromotricyclohexylplumbane (0·032 mole) was then added, and the mixture was stirred at −30° for 30 min. and then at room temperature for 30 min. The usual working-up left a viscous, brown liquid, which was heated at 100°/5 mm. for 30 min. to remove volatile materials, and then taken up in ethanol (50 ml.). The solution was cooled to −20°; it deposited a white solid, which recrystallized from ethanol as needles.

The *methiodide* of tricyclohexyl-*p*-dimethylaminophenylplumbane was obtained by heating the base with a little methyl iodide at 40° for 15 min., and recrystallized from ether–ethanol. This compound was soluble in water and in ethanol, but not in ether. The other aryltricyclohexylplumbanes were soluble in ether and benzene and sparingly soluble in ethanol. All the compounds were decomposed by light.

The properties and yields of the compounds are shown in Table 2. The "decomposition range" denotes the temperature range, which was reproducible, at which the molten liquid decomposed to give a black solid (probably lead).

Cleavage Products (cf. ref. 11).—No attempt was made to isolate a tricyclohexyl-lead perchlorate, but hydrochloric acid was used to show that under acidities greater than those used in the rate studies no cleavage of cyclohexyl-lead bonds occurs. For this, phenyltricyclohexylplumbane (3 g.) was dissolved in boiling ethanol (200 ml.), the solution was cooled to 40°, and 6N-hydrochloric acid (5 ml.) was added. The mixture was set aside for 30 min., then poured into water. The pale yellow solid (2·7 g., 95%) which separated decomposed sharply

[9] Adkins, "Organic Chemistry, An Advanced Treatise" (ed. Gilman), Wiley and Sons Ltd., 2nd edn., New York, 1949, pp. 1071—1072; Gilman, *op. cit.*, pp. 518—520; Rochow, Hurd, and Lewis, "The Chemistry of Organometallic Compounds," Wiley and Sons, New York, 1957, p. 120.

[10] Deans and Eaborn, *J.*, 1959, 2299, 2303; Deans, Eaborn, and Webster, *J.*, 1959, 3031; Eaborn, Lasocki, and Webster, *J.*, 1959, 3034; Eaborn and Webster, *J.*, 1960, 179.

[11] Eaborn and Pande, *J.*, 1960, 1566.

[12] Dessy and Jim-Young Kim, *J. Amer. Chem. Soc.*, 1960, **82**, 686.

[13] Dessy and Jim-Young Kim, *J. Amer. Chem. Soc.*, 1961, **83**, 1167.

[14] Gilman and Dunn, *Chem. Rev.*, 1953, **52**, 77.

[15] Eaborn and Pande, *J.*, 1960, 3200.

at 235° (unchanged by recrystallization from benzene) (Found: Cl, 7·0. Calc. for $C_{18}H_{33}ClPb$: Cl, 7·2%); tricyclohexyl-lead chloride is reported to decompose at 236°.[16]

Similar results were obtained with tricyclohexyl-*p*-tolylplumbane.

Rate Measurements.—The general method has been described.[2–4,10,11]

To 10 ml. of an ethanolic solution of the organolead compound ($4—5 \times 10^{-4}$M, except in the case of the *p*-methoxy-compound) was added 1 ml. of aqueous perchloric acid of strength shown in Table 1. The mixture was shaken, and some of it was transferred to a 1 cm. stoppered cell kept at 25·0° ± 0·03° in a Unicam S.P.500 spectrophotometer, and the optical density relative to a " blank " of ethanol was recorded at suitable time intervals, a wavelength of 300 mμ normally being used.

TABLE 2. *Properties of* $X{\cdot}C_6H_4{\cdot}Pb(C_6H_{11})_3$ *compounds.*

X	Yield (%)	M. p.	Decomp. range	Found (%) C	Found (%) H	Required (%) C	Required (%) H
H	95	146—147° [a]	185—193°	54·1	7·2	54·0	7·2
p-OMe	55	78	176—180	53·6	7·05	53·4	7·15
p-Me	95	97—98	180—185	54·7	7·2	54·8	7·4
p-Cl	60	102—103	166—170	50·9	6·6	50·7	6·6
m-Cl.................	60	73—74	—	50·9	6·8	50·7	6·6
p-NMe_2	78	125	—	54·2 [b]	7·7	54·1	7·5
p-$NMe_3{}^+I^-$	—	185—187 [a]	—	45·1 [c]	6·4	45·3	6·3

[a] With decomp. [b] Found: N, 2·4. $C_{26}H_{43}NPb$ requires N, 2·6%. [c] Found: N, 1·9. $C_{27}H_{46}NIPb$ requires N, 1·8%.

In the case of the *p*-methoxy-compound the concentration of acid was such that with a 5×10^{-4}M-solution of the organolead compound sufficient tricyclohexyl-lead perchlorate was formed to cause a significant removal of acid, and rate constants fell during a run. Use of a 5×10^{-5}M-solution of the lead compound and a wavelength of 230 mμ gave satisfactory results.

It is noteworthy that, whereas in cleavage of aryl–Si, aryl–Ge, and aryl–Sn bonds it was absorption by the aromatic ring which was utilized,[2–4] in cleavage of the lead compounds the absorption due to the lead atom, which is far more intense than that of the aromatic ring in the near-ultraviolet region, is utilized. The optical-density changes were smaller than those employed in the other demetallations, but mean rate constants could be duplicated within 2% from run to run, and the rate constants given in Table 1 are believed to be accurate within ±2%.

We thank the Royal Society for the loan of apparatus. This work was assisted by a grant from the Air Research and Development Command of the U.S. Air Force through its European Office, sponsored by the Aeronautical Research Laboratory of the Wright Air Development Center. We thank Dr. L. Spialter for his interest and encouragement.

THE UNIVERSITY, LEICESTER.

[*Received, March* 17*th*, 1961.]

---

[16] Krause, *Ber.*, 1921, **54**, 2060.