Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

CLEAVAGE REACTIONS OF THE LEAD–CARBON BOND
I. THE REACTION OF TETRAORGANOLEAD COMPOUNDS WITH *N*-BROMOSUCCINIMIDE

BHUVAN C. PANT
Institute for Organic Chemistry TNO, Utrecht (The Netherlands)

(Received April 25th, 1970)

SUMMARY

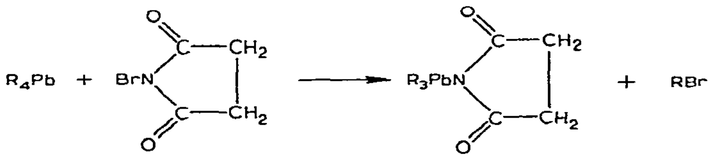
Facile and specific cleavage of lead–carbon bonds has been found to occur when symmetrical and unsymmetrical tetraorganolead compounds are treated with *N*-bromosuccinimide in hydrocarbon solvents. Physical and chemical properties of the *N*-(triorganoplumbyl)succinimides obtained are discussed. An exclusive cleavage of the lead-nitrogen bond was observed in the reactions of *N*-(triorganoplumbyl)-succinimides with acetic acid.

INTRODUCTION

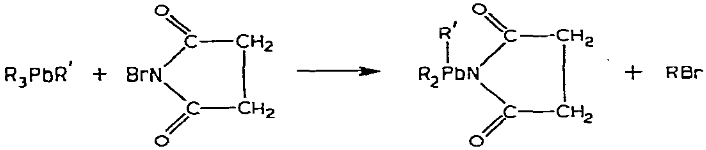
The cleavage of organic groups from both symmetrical and unsymmetrical tetraorganolead compounds by halogens and halogen acids has been studied in detail[1]. After the discovery of tetraethyllead as an antiknock agent various groups of workers studied its reactions with a variety of organic and inorganic reagents obtaining thereby new organolead derivatives and also contributing to the knowledge of the relative stability of lead–carbon bonds[2]. Recently we studied the cleavage of tetraorganolead derivatives with ammonium hexachloroplumbate[3], and the interesting results obtained led us to investigate cleavage reactions using a variety of both organic and inorganic compounds. In an earlier communication[4] we reported the cleavage of an alkyl or aryl group from the corresponding tetraalkyl- or tetraaryllead derivatives using *N*-bromosuccinimide. This paper reports a detailed study of this above type of cleavage.

RESULTS AND DISCUSSION

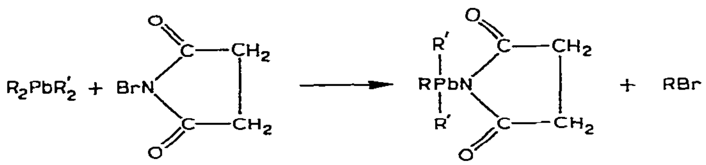
The cleavage of organolead compounds with *N*-bromosuccinimide in hydrocarbon solvents (benzene or toluene) at room temperature may be represented by the following general equations:



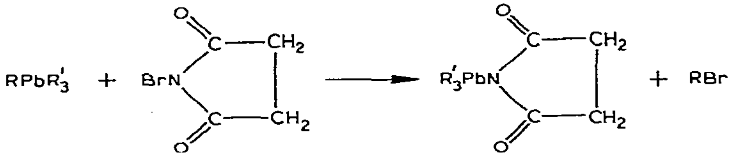
$R = CH_3$, C_2H_5, C_4H_9, C_6H_5, p-$CH_3C_6H_4$ or $2C_4H_3S$



$R = C_6H_5$ or $2\ C_4H_3S$ and $R' = CH_3$, t-C_4H_9 or $C_6H_5CH_2$



$R = C_6H_5$ and $R' = CH_3$



$R = C_6H_5$ and $R' = CH_3$ or i-C_4H_9

N-(Triorganoplumbyl)succinimides obtained in this way are listed in Table 1.

The following orders of ease of cleavage of organic groups from lead by halogens or halogen acids have been established[5,6]:

(*i*). *p*-Tolyl > phenyl > alkyl > benzyl.

(*ii*). 2-Thienyl > phenyl > benzyl.

Similar orders are found for the cleavage of unsymmetrical tetraorganolead compounds by *N*-bromosuccinimide, and there is a high degree of selectivity between the different groups.

It has been reported[7] that dephenylation occurs when tetraphenyltin is treated with *N*-bromosuccinimide in carbon tetrachloride, but no attempts were made to isolate the tin succinimide derivative. A recent communication[8], however, reports

TABLE 1

DATA AND ANALYSES OF *N*-(TRIORGANOPLUMBYL)SUCCINIMIDES[a]

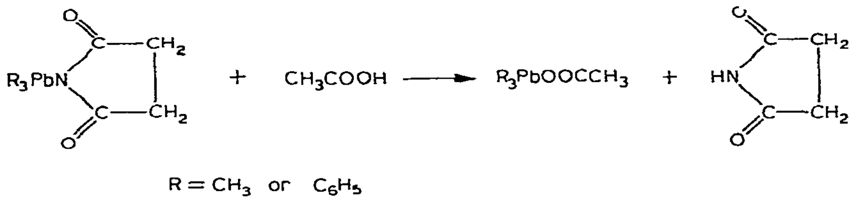
Starting organolead compound	Reaction products		Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)[c]		
	Organic bromide	*N*-(Triorgano-plumbyl)succinimide			C	H	N
$(CH_3)_4Pb$	CH_3Br	$(CH_3)_3PbR$	98	177–178	23.97 (24.00)	3.73 (3.74)	3.79 (3.99)
$(C_2H_5)_4Pb$	C_2H_5Br	$(C_2H_5)_3PbR$	95	74–76	30.96 (30.60)	4.90 (4.88)	3.56 (3.57)
$(2\text{-}C_4H_3S)_4Pb$	$2\text{-}C_4H_3SBr$	$(2\text{-}C_4H_3S)_3PbR$	89	157–158	34.48 (34.60)	2.36 (2.36)	2.51 (2.53)
$(p\text{-}CH_3C_6H_4)_4Pb$	$p\text{-}CH_3C_6H_4Br$	$(p\text{-}CH_3C_6H_4)_3PbR$	97	190–192	51.94 (51.91)	4.43 (4.36)	2.33 (2.42)
$(C_6H_5)_4Pb$	C_6H_5Br	$(C_6H_5)_3PbR$	92	195–197	49.49 (49.24)	3.41 (3.55)	2.58 (2.60)
$(C_6H_5)_3PbCH_3$	C_6H_5Br	$(C_6H_5)_2Pb(CH_3)R$	95	141–144	43.50 (43.03)	3.65 (3.61)	2.94 (2.95)
$(C_6H_5)_3Pb\text{-}t\text{-}C_4H_9$	C_6H_5Br	$(C_6H_5)_2Pb(t\text{-}C_4H_9)R$	87	98–102	46.61 (46.50)	4.51 (4.49)	2.74 (2.71)
$(C_6H_5)_3PbCH_2C_6H_5$	C_6H_5Br	$(C_6H_5)_2Pb(CH_2C_6H_5)R$	85	100–104	49.26 (50.17)	3.86 (3.84)	2.69 (2.54)
$(2\text{-}C_4H_3S)_3PbCH_2C_6H_5$	$2\text{-}C_4H_3SBr$	$(2\text{-}C_4H_3S)_2Pb(CH_2C_6H_5)R$	95	142–144	40.33 (40.55)	3.02 (3.05)	2.41 (2.49)
$(C_6H_5)_2Pb(CH_3)_2$	C_6H_5Br	$C_6H_5Pb(CH_3)_2R$	97	123–125	35.13 (34.99)	3.70 (3.68)	3.65 (3.39)
$C_6H_5Pb(CH_3)_3$	C_6H_5Br	$(CH_3)_3PbR$	97	177–178	24.11 (24.00)	3.70 (3.74)	4.10 (3.99)
$C_6H_5Pb(i\text{-}C_4H_9)_3$	C_6H_5Br	$(i\text{-}C_4H_9)_3PbR$	95	52–54	40.55 (40.32)	6.53 (6.56)	3.15 (2.94)

[a] All these compounds exhibit characteristic absorption bands in their IR spectra including strong carbonyl group bands. [b] R = succinimido. [c] Analyses were carried out at this Institute by Mr. W. J. Buis.

the preparation of *N*-(triorganostannyl)succinimides by the cleavage of tetraorganotin derivatives with *N*-bromosuccinimide. A complex mixture of products was obtained from the reaction of *N*-bromosuccinimide with hexaorganodilead compounds[9]. These reactions are now being reinvestigated under varying reaction conditions, *e.g.* temperature, solvent etc.

Most of the *N*-(triorganoplumbyl)succinimides are fairly stable in air and, with the exception of *N*-(tributylplumbyl)succinimide, possess good hydrolytic stability. *N*-(Triphenylplumbyl)succinimide can be recrystallized from boiling ethanol without solvolysis. The products can be easily purified by recrystallization from boiling acetone or a mixture of n-hexane and benzene. The relatively higher solubility of unsymmetrical *N*-(triorganoplumbyl)succinimides made their recrystallization rather difficult, and freezing of the saturated solution or precipitation with n-hexane was required.

The Pb–N bond in *N*-(triorganoplumbyl)succinimides is cleaved at room temperature by organic acids:



Even in the case of the triphenyl derivative, no phenyl group cleavage was observed with acetic acid. This indicates that the reaction of *N*-(triorganoplumbyl)succinimides with acetic acid proceeds exclusively *via* the cleavage of Pb–N bond. This specificity, coupled with the smoothness of the reaction and the quantitative yields of triorganolead acetates, makes the *N*-(triorganolead)succinimides excellent starting materials for synthesis of pure triorganolead acetates.

EXPERIMENTAL

All the reactions were carried out at room temperature in benzene or toluene. Solvents and *N*-bromosuccinimide (Aldrich) were used as received.

Tetraorganolead compounds were synthesized by conventional methods. The organic bromides formed in the reactions with *N*-bromosuccinimide were characterized by GLC. Melting points are not corrected. The IR spectra were recorded on a Grubb–Parsons Spectromaster. As similar experimental procedures were followed for all the reactions only a few are described as typical examples.

Reaction between tetramethyllead and N-bromosuccinimide

A solution of tetramethyllead (19.2 g; 80% by weight in toluene) was stirred with *N*-bromosuccinimide (10.3 g) in toluene (150 ml) at room temperature. After an induction period of about 35 min an exothermic reaction occurred with the formation of a white precipitate. The mixture was stirred for an additional 5 h. The precipitate was filtered, washed with toluene, and dried under reduced pressure. Recrystallization from boiling acetone gave a white crystalline product (19.7 g; 98% yield).

Reaction between tetraphenyllead and N-bromosuccinimide

A mixture of tetraphenyllead (5.2 g) and *N*-bromosuccinimide (1.8 g) in toluene (200 ml) was stirred at room temperature for 20 h. The precipitate was filtered, washed with toluene, and dried under reduced pressure. Recrystallization from boiling acetone gave pure crystalline product (4.9 g; 92% yield).

Reaction between tri(2-thienyl)benzyllead and N-bromosuccinimide

N-Bromosuccinimide (1.8 g) was added in small portions to a well-stirred suspension of tri(2-thienyl)benzyllead (5.5 g) in benzene (50 ml)at room temperature. An exothermic reaction occurred with the formation of a lemon-yellow colored precipitate. The contents were stirred for 4 h. The precipitate was filtered, washed with benzene and subsequent recrystallization from acetone gave a light-yellow crystalline product (5.3 g; 95% yield).

Reaction between N-(triphenylplumbyl)succinimide and acetic acid

Acetic acid (0.6 g) in benzene (25 ml) was added to a stirred suspension of *N*-(triphenylplumbyl)succinimide (5.4 g) in benzene (50 ml) at room temperature. The contents were stirred for 1 h and the solvent was removed. The residue was extracted with ethanol to remove succinimide. The alcohol insoluble part (4.5 g) was identified as triphenyllead acetate m.p. 204° (lit.[10] 204°–206°).

Reaction between N-(diphenylmethylplumbyl)succinimide and acetic acid

N-(Diphenylmethylplumbyl)succinimide (0.5 g) in benzene (20 ml) was allowed to react with acetic acid (0.06 g) in benzene (10 ml) at room temperature. The residue obtained after removing the solvent was suspended in carbon tetrachloride to remove succinimide. The carbon tetrachloride soluble portion was identified as diphenylmethyllead acetate by its NMR spectrum.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Schrade F. Radtke of the International Lead Zinc Research Organization Inc., New York N.Y. for financial support and Dr. J. G. Noltes of the Institute for Organic Chemistry, TNO, Utrecht for helpful suggestions.

REFERENCES

1 H. Shapiro and F. W. Frey, *The Organic Compounds of Lead*, John Wiley & Sons, New York, 1968, p. 112.
2 R. L. Milde and H. A. Beatty, *Chemical Reactions of Tetramethyllead*, Advances in Chemistry Series, American Chemical Society, Washington D.C., 1957, p. 306.
3 B. C. Pant, *U.S. Patent Application* (to International Lead Zinc Research Organization, Inc., New York, N.Y.), 1969.
4 B. C. Pant and W. E. Davidsohn, *J. Organometal. Chem.*, 19 (1969) P3.
5 E. Krause and O. Schlöttig, *Ber.*, 63 (1930) 1381.
6 H. Gilman, E. B. Towne and H. L. Jones, *J. Amer. Chem. Soc.*, 55 (1933) 4689.
7 E. J. Kupchik and T. Lanigan, *J. Org. Chem.*, 27 (1962) 3681.
8 J. C. Maire, R. Prosperini and J. van Rietschoten, *J. Organometal. Chem.*, 21 (1970) P41.
9 L. C. Willemsens and G. J. M. Van der Kerk, *J. Organometal. Chem.*, 15 (1968) 117.
10 P. R. Austin, *J. Amer. Chem. Soc.*, 53 (1931) 3514.