Tetrahedron Letters No. 10, pp 857 - 860, 1974. Pergamon Press. Printed in Great Britain.

SYNTHESIS OF BIARYLS BY REACTION OF ARYLLEAD(IV) TRICARBOXYLATES WITH AROMATIC COMPOUNDS

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(Received in UK 15 January 1974; accepted for publication 28 January 1974)

In the preceeding communication[1] we reported that aryllead(IV) tricarboxylates react readily at room temperature with trifluoroacetic acid (TFA) to give high yields of aryl trifluoroacetates, and we proposed that aryl cations[2,3,4] are intermediates in these reactions.

In an attempt to trap this proposed reactive intermediate, we have carried out a series of the above reactions in the presence of aromatic compounds in the hope of forming some biaryl derivatives. It can be seen from the results summarized in Table 1, that with some substrates, notably with polymethyl benzenes, the biaryl derivatives form in very high yields. As a wide range of aryllead(IV) tricarboxylates is now readily accessible[1], this reaction forms a convenient synthesis of many biphenyl derivatives.

Consideration of the effect of substituents on the yields of biaryls (Table 1) favours the hypothesis[1] that a positively charged species is indeed an intermediate, formed from the aryllead(IV) substrate. Thus the more highly methylated benzenes, i.e. aromatic compounds with high electron density (entries 1-6 and 11-14, Table 1) are better able to compete with trifluoroacetic acid and give higher yields of biaryl derivatives than less methylated benzenes, and this is confirmed by the results of competitive experiments (entries 8-10, Table 1). Nitrobenzene gave practically no biaryl derivatives (entry 19, Table 1). Where the distribution of isomers was determined (entries 7 and 15-18, Table 1), it was found to be that expected from an electrophilic substituion and not from a radical attack[5]. Also militating against the intermediacy of aryl radicals was the absence of products resulting from attack at methyl groups.

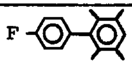
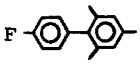
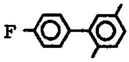
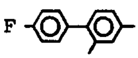
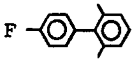
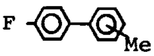
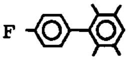
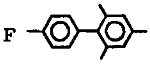
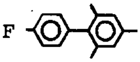
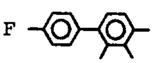
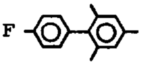
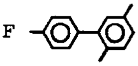
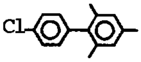
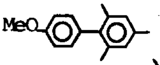
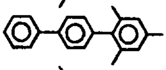
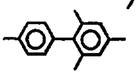
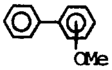
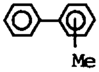
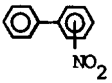
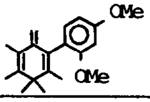
Further evidence for the intermediacy of a cationic species came from the very rapid formation of a triene when hexamethylbenzene was used as a substrate (entry 20, Table 1). The triene clearly arose by a methyl migration in the intermediate cabonium ion, and the n.m.r. spectrum of the reaction mixture prior to work-up showed that an arylhexamethylbenzeneonium ion was present. The stability of this type of ion was first reported by Doering *et al*[6], and more recently the n.m.r. spectrum of a closely related phenylbenzeneonium ion was reported[7].

However, we have evidence that, at least for the more reactive substrates, free aryl cations cannot be intermediates in the formation of biaryl derivatives, because the absolute rates of their formation are greater than the absolute rates of formation of the corresponding aryl trifluoroacetates. Thus the reaction of *p*-fluorophenyllead triacetate with mesitylene in TFA was virtually complete in 15 minutes, whereas the half-time for the conversion of *p*-fluorophenyllead tristrifluoroacetate into the corresponding ester was 90 minutes under the same conditions[1].

We therefore propose that for the more reactive aromatics the formation of the biaryl derivatives proceeds *via* a preliminary π-complex between the aromatic substrate and a species which still has the aryl-lead bond intact[1], and that it is the formation of this complex which lowers the activation energy for the breaking of this bond. Precedent for π-complex formation being a rate determining step in electrophilic substitution can be found in the work of Olah *et al*[8] and, in fact, the results of the competitive experiments with mixtures of substrates (entries 8-10, Table 1) are in good agreement with this hypothesis.

It should be noted that although the distribution of isomers referred to above is consistent with an attack of the aromatic compound on an electron deficient species, the isomer ratios obtained on phenylation of toluene (entries 17 and 18, Table) and anisole (entries 15 and 16) are not identical with those observed by Abramovitch and Gadallah[3] for the phenyl cation generated from the diazonium fluoroborate.

Table 1: Reactions of aryllead(IV) triacetates with aromatic compounds[a]

Entry	Reagent $ArPb(OAc)_3$	Substrate	Conditions	Products (%yield)[b]
	Ar			
1	p-FC_6H_4	durene	*c*	 (67)
2	p-FC_6H_4	mesitylene	*c*	 (88)
3	p-FC_6H_4	mesitylene	*d*	(82)
4	p-FC_6H_4	mesitylene	*e*	(67)
5	p-FC_6H_4	p-xylene	*c*	 (64)
6	p-FC_6H_4	m-xylene	*c*	 (53)  (5)
7	p-FC_6H_4	toluene	*c*	 (2) (*o* 56, *m* 14, *p* 30)
8	p-FC_6H_4	durene & mesitylene (1:1)	*f*	 (67)  (5)
9	p-FC_6H_4	mesitylene & hemimellitene (1:1)	*f*	 (34)  (25)
10	p-FC_6H_4	mesitylene & p-xylene (1:1)	*f*	 (79)  (8)
11	p-ClC_6H_4	mesitylene	*c*	 (75)
12	p-$MeOC_6H_4$	mesitylene	*c*	 (84)[h]
13	p-biphenyl	mesitylene	*g*	 (69)
14	p-MeC_6H_4	mesitylene	*c*	 (72)
15	C_6H_5	anisole	*d*	 (15) (*o* 63.3, *m* 0.6, *p* 36.1)
16	C_6H_5	anisole	*e*	(32) (*o* 47.2, *m* o.4, *p* 52.4)
17	C_6H_5	toluene	*c*	 (10) (*o* 55, *m* 17, *p* 28)
18	C_6H_5	toluene	*e*	(5) (*o* 54, *m* 11, *p* 35)
19	C_6H_5	nitrobenzene	*c*	 (<0.5)
20	2,4-dimethoxyphenyl	hexamethylbenzene	*d*	 (>90)

(Footnotes over page)

Footnotes to Table 1

a All new compounds gave analytical and spectral data consistent with the proposed structures.

b G.L.C. yields unless otherwise indicated.

c TFA (4.0 ml) was added to a mixture of the aromatic substrate (1.0 mmol) and the aryllead triacetate (0.2 mmol).

d TFA (3.0 ml) was added to a solution of the aromatic substrate (1.0 mmol) and the aryllead triacetate (0.2 mmol) in dichloromethane (1.0 ml).

e Dichloroacetic acid (4.0 ml) was added to a mixture of the substrate (1.0 mmol) and the reagent (0.2 mmol).

f TFA (3 ml) was added to a solution of aryllead triacetate (0.2 mmol) and the competing aromatic substrates (2.0 mmol of each) in dichloromethane (1.0 ml).

g Excess TFA was added to a 1:1 mixture of the reactants.

h Isolated yield.

REFERENCES

1. H.C. Bell, J.R. Kalman, J.T. Pinhey, and S. Sternhell, *Tetrahedron Letters*, preceding communication.
2. R.W. Taft, *J. Amer. Chem. Soc.*, 1961, 83, 3350.
3. R.A. Abramovitch and F.F. Gadallah, *J. Chem. Soc. (B)*, 1968, 497.
4. N. Kamigata, M. Kobayashi, and H. Minato, *Bull. Chem. Soc. Japan*, 1972, 45, 2047.
5. D.H. Hey, D.A. Shingleton, and G.H. Williams, *J. Chem. Soc.*, 1963, 5612.
6. W. von E. Doering, M. Saunders, H.G. Boyton, H.W. Earhart, E.F. Wadley, W.R. Edwards, and G. Laber, *Tetrahedron*, 1958, 4, 178.
7. V.A. Koptyug and L.M. Mozulenko, *J. Org. Chem. (U.S.S.R.)*, 1970, 6, 101.
8. G.A. Olah, S.J. Kuhn, S.H. Flood, and J.C. Evans, *J. Amer. Chem. Soc.*, 1962, 84, 3687 and references therein.