Journal of Organometallic Chemistry, 317 (1986) C19–C22
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

ARYL RADICALS FROM ORGANOMETALLIC SOURCES. PREFERENTIAL ATTACK ON THE SIDE CHAIN OF TOLUENES BY THE *o*-TOLYL RADICAL

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(Received August 1st, 1986)

Summary

The *o*-tolyl radicals, formed by the reaction of *o*-chlorotoluene with $[Mo(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) or by the decomposition of *o*-toluoyl peroxide, preferentially attack the methyl group of toluenes giving rise to bibenzyls. In contrast the *m*- and *p*-tolyl radicals preferentially attack the aromatic nucleus.

As reported previously [1,2] the reaction of the dinitrogen complex *trans*-$[Mo(N_2)_2(dppe)_2]$ (I) with aryl halides provides a new and efficient source of aryl radicals. The facile removal of ligated N_2 leads to coordinative unsaturations, so that homolysis of the Ar–X bond can occur, giving rise to halogenomolybdenum complexes and arylated organic products. There is probably an initial charge transfer from Mo^0 to the substrate to give $ArX^{\overline{\cdot}}$ Mo^+, as observed with Ni [3]. A free aryl radical then attacks the aromatic substrate. The resulting adduct (σ complex) is readily aromatized by reaction with a radical $R^\cdot$, and also gives rise to dihydro derivatives as by-products [4]. The type and distribution of the biphenyls thus obtained essentially coincide with those formed in homolytic aromatic substitution processes [4], thus confirming the radical pattern.

Since free aryl radicals are known to attack alkylaromatics mainly at the aromatic nucleus and in part at the alkyl chain [5], we studied the behaviour of the tolyl radicals prepared from I and chlorotoluenes. We have found that the *o*-tolyl radical behaves quite differently from the corresponding *m*- and *p*-radicals and

0022-328X/86/$03.50

from the unsubstituted phenyl radical because it shifts the radical process towards formation of the bibenzyl III (eq. 4, 5), at the expense of the biaryls II (eq. 2, 3).

$$\mathrm{MeC_6H_4Cl} + \underset{\mathrm{(I)}}{[\mathrm{Mo^0}]} \rightarrow \mathrm{MeC_6H_4^{\cdot}} + [\mathrm{MoCl}] \qquad (1)$$

$$\mathrm{MeC_6H_4^{\cdot}} + \mathrm{MeC_6H_4Cl} \rightarrow \underset{(\sigma\cdot)}{[\mathrm{MeC_6H_4(Me)C_6H_4Cl}]^{\cdot}} \qquad (2)$$

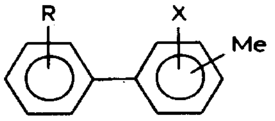
$$\sigma\cdot + \mathrm{R^{\cdot}} \rightarrow \mathrm{HR} + \underset{\mathrm{(II)}}{\mathrm{MeC_6H_4(Me)C_6H_3Cl}} \qquad (3)$$

$$\mathrm{MeC_6H_4^{\cdot}} + \mathrm{MeC_6H_4Cl} \rightarrow \mathrm{MePh} + \mathrm{ClC_6H_4CH_2^{\cdot}} \qquad (4)$$

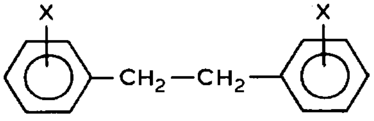
$$2\mathrm{ClC_6H_4CH_2^{\cdot}} \rightarrow \underset{\mathrm{(III)}}{\mathrm{ClC_6H_4CH_2CH_2C_6H_4Cl}} \qquad (5)$$

When a solution of 0.1 mmol of I in 20 ml of *o*-chlorotoluene was kept under reflux for 20 min, bibenzyl III was obtained as the major product, as found by GC/MS analysis (0.19 mol per mol of I, determined by GC with internal standard). Three isomers of II (0.02 mol) and a trace amount of 2,2′-bitolyl were also present (Table 1a). $[\mathrm{MoCl_2(dppe)_2}]$ (0.075 mmol) was isolated from the reaction mixture.

Completely different results were obtained with the *meta* and *para* isomers of chlorotoluene (Table 1, exper. b,c). The total yield of IV + V was comparable, but the ratio between biphenyl IV and bibenzyl V was reversed.



(II : R = Me, X = Cl;
IV: R = H, X = H)



(III : X = Cl;
V : X = H)

To ascertain whether this behaviour was exceptional for free radicals we prepared the phenyl and *o*-tolyl radicals from the corresponding benzoyl and *o*-toluoyl peroxides [6]. The same behaviour was observed for the *o*-tolyl radical, but with lower selectivity, probably as a consequence of the oxidizing power of the aroyloxy radicals [4] and of oxygen when the reaction is carried out in the air (oxygen oxidizes the methyl group extensively, as shown in Table 1, exper. e), and again the unsubstituted phenyl radical preferentially attacked the aromatic ring.

Thus when a 0.02 *M* solution of *o*-toluoyl peroxide in *o*-chlorobenzene was kept at 90°C for 48 h under nitrogen, bibenzyl III (0.15 mol per mol of peroxide) was the major product (Table 1, exper. d). Again three isomers of II were obtained (0.03 mol of II per mol of peroxide), the distribution being identical with that observed from the radicals from the Mo source. Oxidation products of the methyl group such as *o*-chlorobenzyl *o*-toluate (0.07 mol) were also found, together with *o*-toluic acid and *o*-tolyl toluate.

The same reaction under air (Table 1, exper. e) gave 0.03 mol of biphenyls per mol of peroxide and only 0.01 mol of bibenzyl, oxidation products of the methyl

TABLE 1

REACTION OF ARYL RADICALS FROM VARIOUS SOURCES WITH TOLUENES UNDER NITROGEN [a]

Radical sources	Substrate	IV/V molar ratio [b]
(a) I + *o*-chlorotoluene	*o*-chlorotoluene	10/90 [d]
(b) I + *m*-chlorotoluene	*m*-chlorotoluene	83/17 [d]
(c) I + *p*-chlorotoluene	*p*-chlorotoluene	88/12 [d]
(d) *o*-toluoyl peroxide	*o*-chlorotoluene	24/76 [d]
(e) *o*-toluoyl peroxide [c]	*o*-chlorotoluene	77/23 [d]
(f) benzoyl peroxide	*o*-chlorotoluene	71/29 [e]
(g) benzoyl peroxide	*m*-chlorotoluene	87/13 [e]
(h) benzoyl peroxide	*p*-chlorotoluene	85/15 [e]
(i) *o*-toluoyl peroxide	toluene	27/73 [f]
(j) benzoyl peroxide	toluene	68/32 [g]

[a] Radicals from I: 0.01 mmol of I in 20 ml of chlorotoluenes under reflux for 20 min; radicals from peroxides: 90 °C, 48 h, 0.02 *M* solution in the substrate as solvent. Conditions of GLC analyses are described in ref. 2. [b] The two products IV and V are always the major ones, formed along with benzoic or *o*-toluic acid (only when peroxides are used as radical sources). In the reaction under air (e) *o*-chlorobenzaldehyde is the major product because of oxidation of the *o*-chlorobenzyl radical. The amounts of IV are given by the sum of three (toluene) or four (chlorotoluene) isomers. Small amounts of dihydro derivatives were detected by MS, particularly in the case of *p*-chlorotoluene, and are included in the amount of compound IV. [c] Under air. [d] $R = CH_3$, $X = Cl$. [e] $R = H$, $X = Cl$. [f] $R = CH_3$, $X = H$. [g] $R = H$, $X = H$.

group of the substrate being formed instead: *o*-chlorobenzaldehyde (0.09 mol), *o*-chlorobenzyl alcohol (0.06 mol), *o*-chlorobenzyl *o*-toluate (0.01 mol) were identified, along with *o*-toluic acid, its tolyl ester and the lactone of *o*-hydroxymethyl benzoic acid. Similar behaviour was observed when toluene was used as the substrate (Table 1, exper. i, j).

In spite of the low yields of the radicals from the Mo source (in part due to the radical attack at phosphorus mentioned in our previous work [2]) and of those from peroxides (which also are known to give low yields * owing to the presence of heavy products, mainly consisting of tetrahydroquaterphenyls or their derivatives [6,7]), the results appear unequivocal. Since the total yields of biphenyls and bibenzyls are comparable, the larger amount of bibenzyls obtained from the *o*-tolyl radical than from the phenyl radical cannot be attributed to the formation of larger amounts of tetrahydroquaterphenyls, but only to a shift of the site of attack on the alkylaromatic.

The marked selectivity of the reaction of 2-chlorotoluene with the molybdenum complex towards coupling products of secondary radicals is unprecedented in the chemistry of aryl radicals. To find a similar behaviour it is necessary to look to t-butyl radicals, which are known to attack the methyl group of toluenes selectively [8]. In our case the effect must be largely due to steric factors, because 3-chloro- and 4-chloro-toluenes give predominantly the phenylation products.

Strict analogy with the behaviour of the same radical formed by thermolysis of the corresponding aroyl peroxide confirms that the effect is substantially due to the radical structure, the function of the metal being only that of abstracting the

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* Reactions of type 3 can be promoted by using certain additives [7].

chlorine atom. The substrate also has a limited effect in orienting the reaction towards H-abstraction from 2-chlorotoluene, as shown by the experiments in which the phenyl radical is generated from benzoyl peroxide in the presence of chlorotoluenes (Table 1, exper. f, g, h). However, other benzylic compounds, containing other aromatic rings, such as 1-methylnaphthalene and 2,6-chloromethylpyridine, do not show any tendency to give benzyl-type radicals, only phenylation of the aromatic ring taking place. Thus the effects which are at work are rather subtle, and slight variations in the substrates can change the ratio between aromatic substitution and benzylic coupling remarkably.

We conclude that: (i) radicals from the organometallic source $[Mo(N_2)(dppe)_2]$ are true free radicals, whose reactions can be studied without the interference of oxidants; (ii) an *o*-methyl substituent in the phenyl radical exerts a strong influence on the site of attack in an alkylbenzene compound, attack at the benzylic carbon being preferred to that at the aromatic ring.

Apart from the mechanistic implications, which are not be considered here, these features can be relevant to the prospect of designing suitable radicals able to attack benzylic carbon centres rather than the aromatic nucleus.

Acknowledgement. This work was supported by CNR, Progetto Finalizzato per la Chimica Fine a Secondaria.

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