Radical Intermediates in the Reaction of Trityl Esters with Aryl Grignard Reagents

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THE recent Communication[1] indicating the ready reduction of triphenylmethyl (trityl) cation at a dropping mercury electrode prompts us to report our results. Rather than a classical carbanion type of attack by a Grignard reagent on an ester, radical intermediates have been detected in the reaction of several carboxylic esters of triphenylmethanol with aryl Grignard reagents. Trityl acetate (I), benzoate (II), and 2-naphthoate (III) react with aryl Grignard reagents in ether (or ether–benzene) at room temperature during 8 hr. to give highly coloured mixtures. Use of a 1·3 : 1 molar ratio of Grignard reagent to ester resulted in the isolation of trityl peroxide with an average yield of 68% (see Table 1). Analysis of the reaction mixture from (I) by g.l.c. and mass spectrometry revealed a large number of products (see Table 2).

The occurrence of trityl peroxide (IV) and triphenylmethane in the products suggests a trityl radical as a precursor; this was supported by e.s.r. measurements (for type of spectrometer and techniques used see ref. 2) made on the solution of (I) or (II) in ether in the presence of phenylmagnesium bromide. Although a strong signal with broad lines was observed a few minutes after the reactants were mixed, a highly resolved complex spectrum was detectable after about an hour which was very similar to that reported for trityl radical;[3,4] a *para*-coupling of 2·77 G was found in toluene at −20°. The total signal range was 21·5 G with a value of 3·4 G for the strongest coupling constant. Neither (I) nor phenylmagnesium bromide in ether gave an e.s.r. signal; this lack of signal has also been reported for freshly prepared n-butyl Grignard reagent in tetrahydrofuran.[5]

The observations of ion-pair formation with trityl esters[6,7] and the reductive ability of Grignard reagents[5] leads to the following explanation for our results. Electron transfer from the phenyl Grignard reagent to trityl cation to give trityl radical,[1] an acetate, and phenyl radical is not unreasonable. An electron exchange between trityl radical and trityl cation has been reported.[8]

$$\text{(I)} \rightarrow [\mathrm{MeCO_2^{-}{}^{+}CPh_3}] \xrightarrow{\mathrm{PhMgBr}} \mathrm{Ph_3C\cdot} + \mathrm{MeCO_2MgBr} + \mathrm{Ph\cdot}$$

Trityl radical presumably reacts with oxygen in

TABLE 1

Condensation of aryl Grignard reagents with trityl esters

ArM[a] + $RCO_2CPh_3 \rightarrow$ (IV) + other products[b]

Experiments	ArX	R	Molar Ratio ArM: Ester	(IV) Yield (%)
a	PhBr	Me	1·3: 1	72[c]
b	PhBr	Me	4: 1	70[d]
c	*p*-Me-C_6H_4Br	Me	1·3: 1	71
d	*p*-MeO-C_6H_4Br	Me	1·3: 1	69
e	PhBr	Ph	1·3: 1	68[e]
f	*p*-Me-C_6H_4Br	Ph	1·3: 1	65
g	PhBr	2-$C_{10}H_7$	1·3: 1	69
h	*p*-Me-C_6H_4Br	2-$C_{10}H_7$	1·3: 1	64
i	*p*-MeO-C_6H_4Br	2-$C_{10}H_7$	1·3: 1	70

[a] ArM = Aryl Grignard reagent. Experiments a and c were repeated several times and the yields of trityl peroxide (IV) are average figures. Experiments a—d were performed in ether while experiments e—i were done in ether–benzene (1: 1·6, v/v).

[b] G.l.c. revealed a ketone RC(O)Ar as a major product. (A typical complete analysis of a reaction mixture is shown in Table 2.)

[c] Acetic acid [80% based on (I)] was found in the water layer.

[d] The yield of $Ph_2C(OH)Me$ was 70·5%.

[e] Benzoic acid was the only major product found in the water layer by g.l.c.

the ether† to give tritylperoxy-radical which forms (IV) by reacting with another trityl radical. Degassing a solution of (I) in ether with dry nitrogen before addition of the phenyl Grignard reagent resulted in a 4-fold decrease in yield of trityl peroxide and an increase in yield of triphenylmethane. Assuming one equivalent of Grignard reagent is required in the reduction step in the 1·3 : 1 experiment with (I) (see Table 2), only a maximum of 0·3 equivalent of Grignard reagent remains. A model experiment with 2·3 : 1 molar ratio of phenylmagnesium bromide and acetic acid gave acetophenone and 1,1-diphenylethanol. Reaction of excess Grignard reagent with (I) also leads to the same major products (Table 2) including (IV). In addition, the identification of acetic acid in the water layer from the reaction of (I) with phenylmagnesium bromide supports the postulated intermediacy of $MeCO_2MgBr$.

TABLE 2

Quantitative gas chromatographic analysis of reaction mixture resulting from reaction of trityl acetate (I) *with phenylmagnesium bromide* (1: 1·3 *molar ratio*)

Product	Typical yield
Trityl peroxide	60(%)
Acetic acid	80·4
Triphenylmethane	22·5
Acetophenone	14
Benzophenone	12
1,1-Diphenylethanol	<2
Triphenylmethanol	<5
Biphenyl	23
Tetraphenylmethane	1·5
1,1-Diphenylethene	<2

Trityl radical may abstract a hydrogen atom (presumably at the α-position) from ether to give triphenylmethane. Another trityl cation source, trityl bromide, reacted with phenylmagnesium bromide in ether to give (IV), triphenylmethanol, triphenylmethane, benzophenone, and acetophenone. Others have observed trityl peroxide in this reaction but the presence of acetophenone and benzophenone has not been reported.[9] The mechanism of formation of acetophenone is obscure but may also involve attack of a radical on ether.

Benzophenone as a decomposition product of triphenylmethoxy-radicals (probably formed from tritylperoxy-radical) is well documented.[10] When (I) and phenylmagnesium bromide were heated in n-butyl ether at 120—122°, a 2-fold increase in the amount of benzophenone was noted although the yield of (IV) was reduced. Triphenylmethanol probably results from hydrolysis of small amounts of unreacted (I) or by hydrogen abstraction by the triphenylmethoxy-radical.

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† A recent observation indicates that the tritylperoxy radical exists in equilibrium with trityl radical and oxygen; see C. L. Ayers, E. G. Janzen, and F. J. Johnston, *J. Amer. Chem. Soc.*, 1966, **88**, 2610; E. G. Janzen, F. J. Johnston, and C. L. Ayers, *ibid.*, 1967, **89**, 1176.

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