

ELECTRON TRANSFER REACTIONS INVOLVING TRITYL BROMIDE AND PHENYLMAGNESIUM BROMIDE. RADICAL INTERMEDIATES FROM DIETHYL ETHER AND DI-N-PROPYL ETHER

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Trityl bromide and phenylmagnesium bromide react via an electron transfer process to give radical intermediates which react with the solvents diethyl ether and di-n-propyl ether.

Ion pair formation of trityl esters (1, 2) and the reducing ability of Grignard reagents (3) are well known. Based on these previous observations and by using $\text{CH}_3\text{C}^{18}\text{O}_2\text{C}(\text{C}_6\text{H}_5)_3$, we were led to postulate a novel electron transfer process in the reaction of phenylmagnesium bromide (formula 1) and trityl acetate (4, 5). We had observed in preliminary experiments that trityl bromide (formula 2) in diethyl ether reacted with formula 1 at room temperature to give triphenylmethane (formula 3) and several other products (4, 5). We have examined this reaction and conclude that *diethyl ether participates*. Acetophenone was the major product previously inferred (4, 5) as indicative of the participation of diethyl ether in the reaction. It has now been confirmed by mass spectra and pmr analysis that this component is really 1-phenylethanol (formula 10). The confusion arose because of the essentially identical retention times of acetophenone and formula 4 on several glpc columns employed in the analysis.

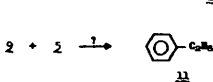
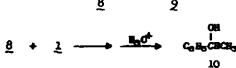
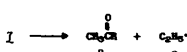
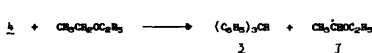
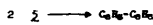
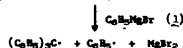
METHODS

For standardization purposes, more than a dozen separate preparations of phenylmagnesium bromide (formula 1) in diethyl ether were examined for content (up to a 24-hr period) after hydrolysis (0.6 N HCl). Analyses were performed on two separate glpc units, namely an Aerograph 1520B with hydrogen flame detector and an Aerograph 1700 with thermal conductivity detector. The data from fifteen separate experiments was reproducible to $\pm 2\%$. Mass spectral analysis was obtained on a unit previously described (6).

RESULTS AND DISCUSSION

Glpc analysis revealed only traces

(<0.5%) of products other than benzene. When trityl bromide (formula 2) (0.03 mole) was added to a large excess of formula-1 (0.24 mole), glpc, mass spectral, and pmr analysis indicated the presence of triphenylmethane ($\approx 5\%$), biphenyl (2-3%), 1-phenylethanol ($\approx 1.5\%$) and ethylbenzene ($\approx 1\%$) as well as benzophenone, and triphenylmethanol previously identified (1.5 hr total reaction time — overall conversion of formula 2 <10%). Triphenylmethanol was always the major product (<90%) resulting from hydrolysis of unreacted formula 2. If the mixture was allowed to stand in air or if oxygen was added, trityl peroxide was formed (4, 5). A mechanism most consistent with these results is:

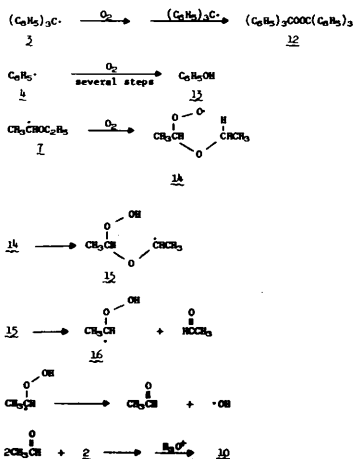


It was found that the yield of products was not altered if the reaction was run under N_2 . The coupling of ethyl radical

(formula 9) with phenyl radical (formula 5) is defended on the following grounds. In the dilute solution, the probability of two ethyl radicals homocoupling or undergoing disproportionation must be small. Therefore heterocoupling with phenyl radical can occur. This *cross termination* process is not without precedent (7). *The identification of ethylbenzene and 1-phenylethanol definitely establishes the participation of diethyl ether in the radical reaction.*

In view of the previous results, we elected to add oxygen at intervals to the reaction mixture in an effort to retard formation of 1-phenylethanol by removal of trityl radical. After trityl bromide was added, the solution was stirred for 15 min. Oxygen (100 ml/min) was bubbled in for 5 min. A sample was hydrolyzed and analyzed. After 25 min, oxygen was again added to the mixture for 5 min and again a sample was removed, hydrolyzed, and analyzed. This process was repeated every 30 min for a total of 3 hr.

Although the yield of formula 3 was reduced, surprisingly the yield of 1-phenylethanol (formula 10) was increased by a factor of two. As expected, trityl peroxide (formula 12) formed in addition to formulas 5 and 6, and phenol (formula 13). A tentative mechanism is:



Decomposition of the suggested hydroperoxy radical intermediate (formula 16) could find considerable driving force in the generation of the carbonyl group (8). Regarding decomposition of the hydroperoxide of diethyl ether, acetaldehyde has been suggested as one initial product (9). Thus, decay of formula 14→ formula 15→ formula 16→ CH₃CHO may be reasonable. Thus, the increased yield of formula 10 in the "oxidation" reaction probably results from ether oxidation. This process offsets the effect of decreasing the concentration of "hydrogen abstracting" radicals (namely, (C₆H₅)₃C· and perhaps C₆H₅·) which are required for the production of formula 7.

Our results find some analogy with the data of W. V. Evans and coworkers (10-12). They found that the electrolysis of propylmagnesium bromide in diethyl ether gave 2-pentanol via decomposition of formula 7 to acetaldehyde which was attacked by the Grignard reagent.

Di-*n*-propyl ether substituted into the reaction with formula 1 and formula 2 (with and without O₂ added) gave identical products except that 1-phenylpropanol was the alcohol identified. Thus a mechanism similar to that with diethyl ether is probable.

We suggest that the absence of β-protons (beta to the carbon carrying the charge in (C₆H₅)₃C⁺), the ease of reduction of trityl cation (for example at the dropping mercury cathode) (13), and the difficulty in forming the hindered tetraphenylmethane from trityl cation and formula 2 may force the electron transfer to occur in the work described. At the short reaction times employed at room temperature, tetraphenylmethane could not be detected in the reaction mixture.

Radical intermediates in Grignard reactions are not especially common (except, of course, when cobaltous chloride, azoxy compounds, etc. are present) but are not unknown (14, 15). Recently published data appear to involve an electron transfer process (14-16). A suggestion was made for participation of THF in the reaction of neopentylmagnesium chloride with benzophenone (14, 15). Ethyllithium and trityl chloride are recorded to give trityl radicals (14, 15).

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