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ANODIC TRIFLUOROACETOXYLATION OF METHYLBENZENES.

A NOVEL CATION RADICAL STABILIZATION.

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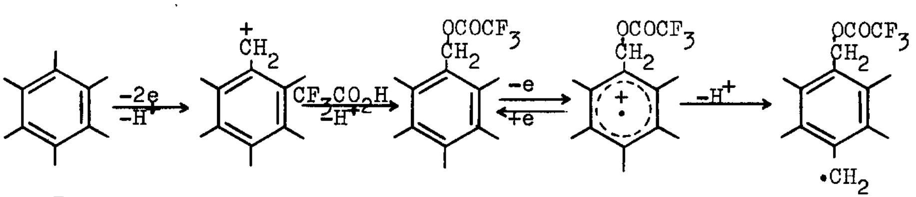
The formation of carbon oxygen bonds during anodic substitution processes such as hydroxylation, methoxylation and acetoxylation generally results in the formation of initial products more easily oxidized than the substrates (2). This complication severely limits the application of anodic substitution as a synthetic method as well as prohibits the use of such quantitative techniques as coulometry to study these reactions. Here we report an anodic substitution reaction in which carbon oxygen bonds are formed but which yields a product substantially more difficult to oxidize than the substrate and thus allows for the high yield isolation of the initial oxidation product and renders the reaction susceptible to coulometric study.

Cyclic voltammetry of hexamethylbenzene in trifluoroacetic acid or methylene chloride - trifluoroacetic acid (9-1) showed that two electrons are transferred in the first irreversible oxidation peak (+1.32 V. vs SCE) and revealed a second oxidation peak (O_2) at +1.64 V. On the cathodic going sweep, a reduction peak (R_2) was observed corresponding to reduction of the species formed at O_2. Constant current coulometry (3) showed that 2.0 Faradays per mole were consumed and voltammetry of the resulting solution showed a quasi-reversible oxidation-reduction couple at the same potential as O_2-R_2 of the solution before coulometry. Preparative electrolysis of hexamethylbenzene in the same medium resulted in the nearly quantitative formation of the trifluoroacetoxylation product (III). These results are in accordance with the Scheme. The first step is apparently a 2e oxidation to the benzyl cation (II) which solvolyzes to III. The cation radical of hexamethylbenzene is evidently very short lived in trifluoroacetic acid or in the mixed solvent since we were unable to detect a reduction peak by cyclic voltammetry. On



I II III IV V

SCHEME

the other hand, IV is relatively stable in both the latter media showing a reduction peak at the slow sweep rate of 150 mV/sec. Both voltammetry and coulometry of pentamethylbenzene and durene are exactly analogous to that observed for hexamethylbenzene. The ratio of cathodic to anodic peak currents for the latter radical ions was less than that for IV indicating less stability.

The stabilization of IV due to the presence of the trifluoroacetoxy group is indeed surprising. It is a well known fact that electron donating groups such as methoxy or dimethylamino have profound stabilizing influence and this is due to structures in which the positive charge can be written on the hetero atom. This is to our knowledge the first case of stabilization by a strong electron withdrawing group. The fact that III is oxidized 320 mV more anodic than I reflects this strong electron withdrawing effect. The most likely reaction of IV is deprotonation to give V. The pK_a of phenol cation radicals have been estimated to be about -5 (4) and IV would surely be an even stronger acid which makes the cation radical stabilization by CF_3CO_2 even more surprising.

Our results indicate that the hexamethylbenzene cation radical is very short lived in trifluoroacetic acid. This suggests that the recently reported observation of the esr spectrum of the latter ion radical (5) in trifluoroacetic acid may be erroneous and the radical actually observed may have been IV. Further work is in progress both on the anodic trifluoroacetoxylation of aromatic compounds and the stabilizing effect of the trifluoroacetoxy group on cation radicals.

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