The Influence of a Substituent with Free Radical Character (Reverse Effect) on Some Nucleophilic Substitutions involving Benzylic Systems

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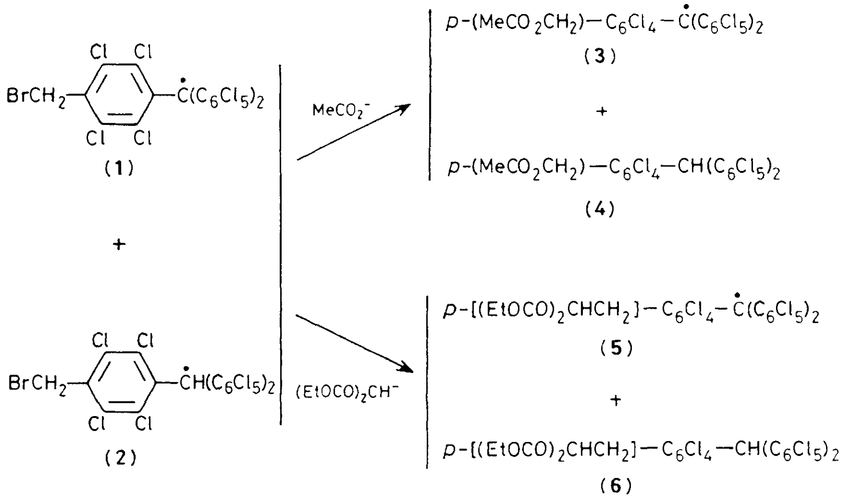
The free radical character of the benzyl bromide (1) causes accelerations in the nucleophilic substitution reactions with acetate and with diethyl malonate anions which are interpreted in terms of a charge-transfer, biradical configuration for the *S*N2 transition state.

The influence of the substituents on the reactivity of free radicals has been investigated extensively. With the discovery of *inert free radicals*,[1] the study of the opposite effect: *i.e.*, the influence of the free radical character in a molecule on the reactivity of its non-radical substituents, has become possible. A few results on this new effect (the *reverse effect*) have recently been announced.[2]

We now report the first results on the reverse effect involving nucleophilic substitutions, the substrate being the 4-(bromomethyl)tetradecachlorotriphenylmethyl radical (**1**), an inert free radical of the PTM (perchlorotriphenylmethyl) series.[1]

Two competitive nucleophilic-substitution reactions with an equimolar mixture of the benzyl bromide (**1**) and its non-radical analogue (**2**) were carried out. The acetoxylation with sodium acetate (large excess) in MeOH–dioxane (66 °C) gave a mixture of acetates (**3**) and (**4**). The reaction with the diethyl malonate carbanion (excess of malonate diester and K_2CO_3) in dioxane (90 °C) resulted in a mixture of malonate derivatives (**5**) and (**6**). From the data obtained, it was concluded that radical (**1**) reacts faster than its non-radical analogue (**2**)



by a factor of about 4, with acetate, and 9, with malonate.

A current quantum mechanical approach constructs the S_N2 transition state as a combination of a few main electronic configurations for the system formed by the reactants (the nucleophilic reagent D^- and the substrate A), the most significant one being the charge-transfer, biradical configuration $D{\cdot}A^{\bar{\cdot}}$ resulting from an electron jump from D^- to an empty (σ^*) orbital of A.[3] Therefore, in the *reverse effect* studied here, it is expected that interactions of such a biradical configuration with the SOMO of the free radical would cause an additional stabilization of the transition state; *i.e.*, an increase in the rate of the nucleophilic substitution, as observed.

Products (**3**)—(**6**) have been synthesized separately and fully characterized.

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