

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

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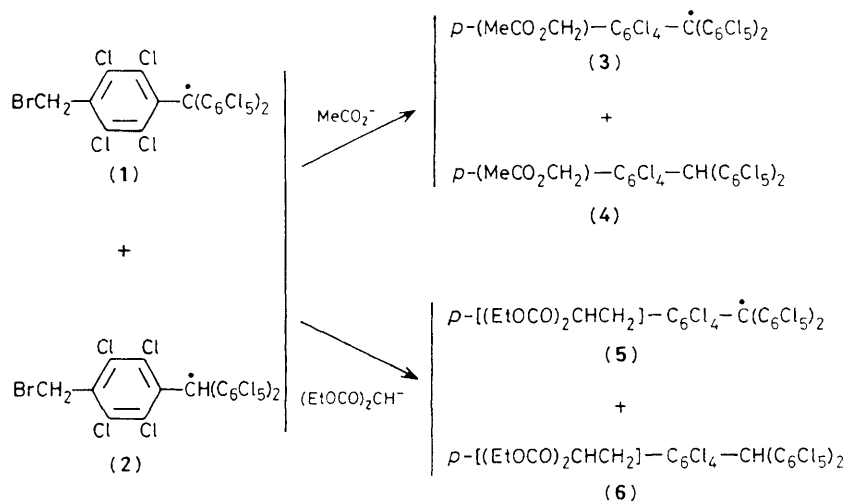
The free radical character of the benzyl bromide (1) causes accelerations in the nucleophilic substitution reactions with acetate and with diethyl malonate anions which are interpreted in terms of a charge-transfer, biradical configuration for the S_N2 transition state.

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-(bromo-methyl)tetrachlorotriphenylmethyl 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 $D\cdot A\cdot$ 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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