LETTERS TO THE EDITOR

HOMOLYTIC FISSION OF THE C—C BOND IN A σ-COMPLEX CORRESPONDING TO A NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN A HETEROAROMATIC CATION

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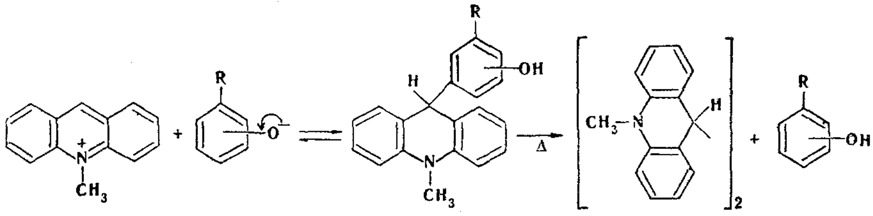
The homolytic dissociation of a C—C bond in solution is an extremely rare phenomenon and has only been described for derivatives of polyarylethane, certain pinacones, and lucigenin derivatives [1]. Homolysis of a C—C bond or any other bond formed between an electrophile and a nucleophile in σ-complexes of nucleophilic aromatic substitution has not been observed previously although heterolytic fission of such bonds is widely known.

In the present work homolytic splitting was detected for a C—C bond in adducts (IIIa-c) which were formed on adding phenols to the acridine cation (I) and which may be considered as σ-complexes. The formation of compounds (III) was recorded in a series of cases in the PMR spectra of solutions of reaction mixtures of cation (I) and phenols [2]. It is also possible to obtain them by the interaction of cation (I) and phenolate anions (IIa-c) in a dry aprotic solvent:



I IIa-c IIIa-c IV Va-c

phenolates IIa-c: a — phenol, b— *o*-cresol, c — 1-naphthol

The constitution of substances (IIIa-c) was demonstrated by data of IR and PMR spectra and also by converting them into O-actyl derivatives.

On heating compounds (IIIa-c) in an aprotic solvent in an argon atmosphere at 130-150°C N,N-dimethyl-9,9-diacridanyl (IV) was formed which was identified by data of elemental analysis, IR and PMR spectra. Thus after heating at 130°C in xylene 10-methyl-9-[2'-(1-hydroxynaphthyl)]acridane (IIc) precipitated 5% dimer (IV) from solution. The initial compound (IIIc) and naphthol (Vc) were also isolated from the reaction mixture. According to TLC there were still three substances in the reaction mixture which have not so far been identified.

The homolytic character of the fission of compounds (IIIa-c) was confirmed not only by the formation of dimer (IV) but also by ESR spectra of xylene solutions of compound (IIIc). The direct observation of the acridinyl radical was not possible due to its instability. The recording of hydroxynaphthyl radicals also failed at high temperatures. The formation of radical particles was confirmed by the use of compounds generating stable radicals on radical attack. On heating acridane (IIIc) with diphenylpicrylhydrazine in xylene solution an ESR signal was observed for the diphenylpicrylhydrazine radical (characteristic five-component spectrum). The ESR signals were also recorded in a similar experiment with tri-tertiary butylphenol. The resulting radicals were not formed as a result of side reactions of oxidation, which may be caused, e.g., by the presence of oxygen contaminants in the argon. In blank experiments heating diphenylpicrylhydrazine and tri-tertiary butylphenol for 45 min in xylene without acridane (IIIc), the ESR signals were not recorded.

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FREE RADICAL AMIDOMETHYLATION OF INDOLES WITH AZOMETHINES IN THE PRESENCE OF ACYLATING AGENTS AND ZINC DUST

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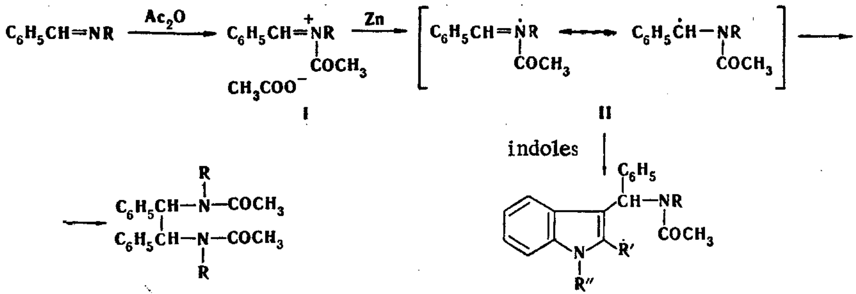
We have found that on reacting zinc dust with the N-acylimmonium cation (I), obtained by the interaction of azomethines with acylating agents, the radicals (II) are formed which recombine but on adding nucleophilic aromatic or heterocyclic compounds to the reaction medium they may act as amidomethylating agents.



IVa-e

Thus we obtained diaminoethane derivatives (III) and 3-amidoethylindoles (IVa-e) from azomethines and indoles. For the products: R, R', R', mp, °C: a) C_6H_5, H, H, 150-152; b) CH_3, H, H, 146-148; c) CH_3, CH_3, H, 184-186; d) CH_3, H, CH_3, 97-99; e) C_6H_5, H, CH_3, 93-95. The structure of indoles (IV) were confirmed by elemental analysis and IR spectra.

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