REACTION OF THE TRIPHENYLVERDAZYL RADICAL WITH BENZOTRICHLORIDE

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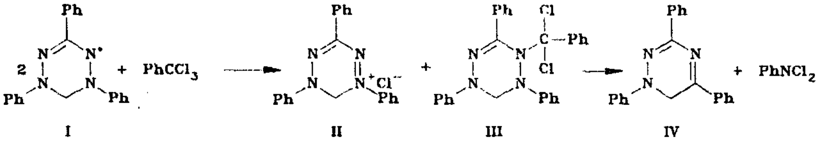
Stable triphenylverdazyl radicals are used as internal indicators in the study of the kinetics of the monomolecular heterolysis of organic compounds [1]. Additional information regarding the mechanism of the reaction is obtained in the identification of the products formed via the reaction of the cationoid intermediate (the product of the rate-determining step) with the triphenylverdazyl radical (I). We have found that the monomolecular heterolysis of benzotrichloride in solution in acetonitrile ($v = k[PhCCl_3]$) in the presence of radical I leads to the formation of 1,3,5-triphenyl-1,6-dihydro-1,2,4-triazine (IV) and triphenylverdazylium chloride (II), the concentration of which is equal to half the amount of radical I consumed in the reaction. Triazine IV is evidently formed as a result of recyclization of III — the product of alkylation of radical I by the cationoid intermediate that develops in the heterolysis of $PhCCl_3$. The formation of phenyldichloroamine was not proved.



The assumption regarding the intermediate formation of phenylchlorocarbene and its subsequent reaction with radical I or salt II is not adequate to explain the formation of triazine IV, since neither dichlorostilbene (the product of dimerization of $Ph\ddot{C}Cl$) nor PhCOCl (the product of the reaction of $Ph\ddot{C}Cl$ with oxygen) was detected in the reaction mass by gas-liquid chromatography.

The half-conversion time of $PhCCl_3$ in MeCN at 25°C is 1.5 yr, and $k \approx 1.2 \cdot 10^{-8}$ sec^{-1}.

A solution of 3 mmole of $PhCCl_3$ and 12 mmole of radical I in 50 ml of MeCN was maintained at ~60°C in a sealed ampul for 6 months, after which the solvent was removed by distillation, and the residue was treated with warm benzene. The mixture was filtered to give 1.3 g of an undissolved dark-brown substance, which was identified as the product of the reaction of radical I with salt II [2]. The benzene extract was evaporated in vacuo, and the residue was chromatographed on silica gel L (100/250 μ) (50 cm) by elution with benzene. The eluate was collected in the form of several colored fractions. The solvent was removed from the bright-green fraction by distillation, the residue was triturated with ethanol, and 0.16 g (20%) of triazine IV in the form of a light-yellow finely crystalline substance with mp 176-178°C (dec., from benzene—ethanol) was removed by filtration. IR spectrum (KBr): 1640 (C=N) and 2880 cm^{-1} (CH_2). UV spectrum (in MeCN): λ_{max} 400 nm. PMR spectrum (in CCl_4): 6.3-6.8 (m, 15H, aromatic); 4.1 and 5.1 ppm (2H, CH_2, dd, J = 11 Hz). The results of elementary analysis for C, H, and N were in agreement with empirical formula $C_{21}H_{17}N_3$: M (Rast method) 330 ± 30; calculated M 311.4.

LITERATURE CITED

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