$CHCl_3$ cooled to -20 °C. The reaction mixture was allowed to stand at 20 °C for 2 h in the case of indole and 2-methylindole or for 24 h in the case of 1-methyl-2-phenylindole. The solvent was evaporated in vacuo, and the residue was crystallized from hexane. The physicochemical characteristics of II-IV are presented in Table 1.

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EFFECT OF AN EXTERNAL MAGNETIC FIELD ON PHOTOLYSIS OF

AQUEOUS SOLUTIONS OF CYCLOHEXANONE

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The effect of an external magnetic field on the ratio of the yields of the basic products of photolysis of aqueous solutions of cyclohexanone was investigated by high-resolution NMR spectroscopy. It was shown that the magnetic field does not significantly affect the yield of the products of the reaction with a 0.2 M concentration of the starting ketone, the yield of 5-hexenal decreases, and the yield of caproic acid and the rate of photolysis increase below 0.02 M. The observed effects are explained by association of cyclohexanone with involvement of the HFI mechanism from the theory of "radical pairs."

Photolysis of solutions of cyclohexanone have been investigated in some detail both by standard kinetic methods [1] and with the effect of chemical polarization of nuclei (CPN) [2]. It was found that α -rupture from the triplet electron state with subsequent recombination or disproportionation of the triplet biradical formed primarily takes place under the effect of light [3]. Disproportionation can take place simultaneously along two paths with formation of unsaturated aldehyde and ketone, which easily yields adducts with a solvent [4]. Based on a study of the field dependences of the CPN effects, it was shown in [5] that the aldehyde and adduct sometimes have different polarization signs and for this reason, using the terminology of the theory of radical pairs, the adduct can be considered as the product of emergence from the "cage."

The dependence of the yield of products of photolysis of aqueous solutions of cyclohexanone on the strength of the external magnetic field predicted by the results of studies of the effects of CPN and the appearance of a magnetic isotope effect (MIE) [6], was investigated.

EXPERIMENTAL

Photolysis of 0.2, 0.02, and 0.002 M solutions in D_2O was investigated. The reaction was conducted at 293 K in 5-mm quartz ampuls using the light from a DRSh-500 lamp passed through a heat filter. The irradiation time was 30 min for the 0.2 and 0.02 M solutions

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| | 0,2 M | | 0,02 M | | |
|--|-------------------------------------|-------------------------------------|--------------------------------------|--------------------------------------|--|
| Products | 5.10-5 | 0,13 | 5.10-5 | 0,13 | |
| | T | | T | | |
| $C_{6}H_{10}O * CH_{2} = CH - (CH_{2})_{2} - CH(O) CH_{3} - (CH_{2})_{4}C(O) OD ** C_{1}/C_{3} ** C_{2}/C_{3}$ | 58,0 12,1 9,8 5,92 1,23 | 58,0 12,1 9,8 5,92 1,23 | 35,8 19,1 23,9 1,50 0,80 | 34,4 18,0 25,6 1.34 0,70 | |

TABLE 1. Yield of Basic Products of Photolysis of Aqueous Solutions of Cyclohexanone

*Estimated with the concentration of the double bonds. **Ratio of the yields of products. Relative error of measurements of the yield of products of ~3%.

and 5 min for the 0.002 M solution. The products of photolysis were analyzed by NMR spectroscopy on BS-567A and WM-360 spectrometers. The results of the measurements were processed by the method of least squares. The relative error of measurement of the yields of the products of photolysis of the 0.2 and 0.02 M solutions was 3%. We were unable to measure the yield of products of photolysis for the 0.002 M solutions with a high degree of precision; for this reason, we will not report them and will only indicate the tend, ency observed in the discussion of the results. The magnetic field was created with barium hexaferrite plates. The homogeneity of the magnetic field was not monitored. The area of the plate was 96 cm². The maximum field strength in the 2-cm gap between plates was 0.13 T.

RESULTS AND DISCUSSION

We previously studied the MIE on the products of photolysis of cyclohexanone [7]. It was found that the efficiency of separation of isotopes is strongly dependent on the degree of conversion and initial concentration of ketone. For this reason, we investigated solutions of different concentrations.

The yields of products of the reactions as a function of the conditions of photolysis are reported in Table 1.

The experimental data show that the magnetic field affects the ratio of products formed during photolysis for a starting 0.02 M concentration of cyclohexanone and has no effect for a 0.2 M concentration within the limits of the error of the measurements. The ratio of the concentrations of cyclohexanone and caproic acid in the solution after irradiation in the magnetic field decreased by 11%, and the ratio of the concentrations of aldehyde and acid decreased by 13%. Similar changes were also observed for the 0.002 M solutions. Decreasing the external field to 0.01 T produces an effect almost identical to the effect observed in the 0.13 T field.

The results of these studies and the results obtained in studying the appearance of the MIE in the products of photolysis of aqueous solutions of cyclohexanone are satisfactorily correlated [7]. In both cases, the magnetic effects are significantly manifested for relatively low concentrations of the starting ketone.

It is necessary to note that the CPN and MIE effects and our results were obtained for comparable initial concentrations of cyclohexanone.

In our opinion, very significant magnetic effects in photolysis of cyclohexanone should not be expected, since the biradical formed during photolysis has an insignificant length in the "stretched" state (configuration) and consequently a large exchange reaction so that the effect of the hyperfine interaction on intercombination transitions (i.e., also the possible magnetic effects) is decreased. The relatively weak effect of the magnetic field can also be due to the fact that only some of the cyclohexanone decomposes according to the biradical mechanism. The lack of an effect of the magnetic field on the yield of products for a high concentration of cyclohexanone is perhaps determined by the effective competition of concentration quenching of photoexcited cyclohexanone molecules with intercombination transitions.

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Cu(I) COMPLEXES WITH OLIGO- AND POLYARYLENE PHOSPHITES

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Monovalent copper complexes with oligo- and polyarylene phosphites were obtained. Complexation takes place due to coordination of copper with the phosphorus atom.

The advances in the study of the synthesis, properties, and use of metal complexes based on trivalent phosphorus derivatives as homogeneous catalysts are well known [1, 2]. Data have recently been published on the preparation and use of polymeric compounds containing fragments of metal complexes of the phosphine and phosphite types in their structure in catalysis [3]. It is very important that such high-molecular-weight coordination com-

| Complex Yield, | | Found/Calculated, % | | | ^{3 1} P NMR spectrum (benzene) | | |
|----------------|------|----------------------------|-----------------------|--|---|-------|--|
| | | | Empirical | δP | ΔδΡ | | |
| | Ϋ́υ. | Р | Cu | [UIIIIIa | ppm | | |
| (1) | 87 | 8,71 | <u>17.90</u> 18.01 | C10H16BrCuNO2P | 102,7 | -39,4 | |
| (II) | 85 | $\frac{7,62}{7,69}$ | <u>15,72</u> 15,76 | C14H18BrCuNO2l' | 112,5 | -29,3 | |
| (111) | 82 | 8.56 | <u>17,62</u> 17,72 | Cu ₁₄ H ₁₆ ClCuNO ₂ P | 114,7 | -25,3 | |
| (IV) | 83 | $\frac{6,97}{7,05}$ | <u>14,35</u> 14.44 | C ₁₆ H ₁₁ BrCuO ₃ P | 98,4 | -31,1 | |
| (V) | 80 | $\frac{7,75}{7,84}$ | <u>15,98</u> 16,06 | C16H11ClCuOsl' | 104,0 | -25,5 | |
| (VI) | 81 | 7.61 | <u>15,67</u> 15,77 | C14H18BrCuNO2P | 114,6 | -26,8 | |
| (VII) | 85 | <u>6,70</u> <u>6.79</u> | <u>13,82</u> 13,91 | C ₁₈ H ₂₀ BrCuNO ₂ P | 125,6 | -23,2 | |

TABLE 1. Cu(I) Complexes with Oligo- and Polyarylene Phosphites and Polyarylene Amidophosphites

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