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SYNTHESIS OF ESTERS OF IMINOCARBONIC ACID

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The first syntheses of asymmetrical esters of iminocarbonic acid are reported. These syntheses were carried out without the separation of intermediates.

Esters of iminocarbonic acid are promising reagents in organic synthesis. However, their application is limited by the lack of convenient synthetic methods. The most well-known method for the preparation of iminocarbonic acid esters is based on the chlorination of alcoholic solutions of transition metal cyanides with subsequent reduction of the chloroiminocarbonic acid esters obtained using alkali metal arsenites [1].

We carried out the syntheses of symmetrical and asymmetrical esters of iminocarbonic acid by the reaction of an alkali metal alcoholate with cyanogen bromide

$$\mathrm{RONa + BrCN + R^1OH \rightarrow \underset{I(a-\ell)}{ROCNHOR^1} + NaBr}$$

EXPERIMENTAL

The iminocarbonic acid esters were synthesized by two methods.

Method A: Preparation of Symmetrical Iminocarbonic Acid Esters (Ia)-(If). A sample of 0.1 mole BrCN in THF was added dropwise with rapid stirring and cooling to a solution of 0.1 mole alkali metal in excess alcohol at a rate such that the temperature of the reaction mixture did not exceed 5°C. The precipitate formed was filtered and washed with THF. After distillation of the THF, the residue was distilled in vacuum.

Method B: Preparation of Symmetrical and Asymmetrical Iminocarbonic Acid Esters (Ig)-(Iℓ). A solution of 0.1 mole BrCN in dry THF was added dropwise with rapid stirring and cooling to a suspension or solution of 0.1 mole alkali metal alcoholate in dry THF at a rate such that the temperature of the reaction mixture did not exceed 5°C. After all the reagent was added, the reaction mixture was brought to ~20°C and 0.1 mole alcohol was added dropwise. The precipitate formed was filtered and washed with dry THF. The solvent was removed and the residue was distilled in vacuum. The yield and physical indices of the products are given in Table 1.

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TABLE 1

Compound	R	R^1	Yield, %	Bp, °C (p, mm Hg), mp, °C	n_D^{20}
(Ia)	CH_3	CH_3	50	102–105 (320)	1,4092
(Ib)	C_2H_5	C_2H_5	80	40 (12)	1,4170
(Ic)	$n-C_3H_7$	$n-C_3H_7$	80	61 (6)	1,4208
(Id)	$i-C_3H_7$	$i-C_3H_7$	69	41–42 (7)	1,4120
(Ie)	$n-C_4H_9$	$n-C_4H_9$	70	83–84 (5)	1,3902
(If)	C_6H_5	C_6H_5	95	53–54	–
(Ig)	CH_3	C_2H_5	68	20 (12)	1,4190
(Ih)	CH_3	$n-C_3H_7$	75	45 (15)	1,4150
(Ii)	CH_3	$n-C_4H_9$	78	51 (5)	1,4197
(Ij)	C_2H_5	$n-C_3H_7$	75	45 (6)	1,4208
(Ik)	C_2H_5	$n-C_4H_9$	84	57 (6)	1,4236
(Iℓ)	$n-C_3H_7$	$n-C_4H_9$	90	73 (6)	1,4269

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ISOTOPE EFFECT IN THE GAS-PHASE PHOTOLYSIS OF CYCLOHEXANONE

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An isotope effect was found for the carbonyl and α-carbon atom in the gas-phase photolysis of cyclohexanone, which is apparently magnetic in nature. This finding additionally indicates that the chemically induced dynamic nuclear polarization in the gas phase in the photolysis of cyclohexanone arises predominantly in biradicals and not in triplet molecules. The separation of isotopes occurs more efficiently in the photolysis of aqueous solutions of cyclohexanone than in the gas phase.

The study of the effects of chemically induced dynamic nuclear polarization (CIDNP) in the photolysis of cyclic aliphatic ketones in solution [1] and in the gas phase [2] showed that the major reason for the generation of nonequilibrium nuclear polarization in both cases is singlet–triplet evolution in the biradicals formed. However, an alternative mechanism exists involving optical nuclear polarization [3], which may give a significant contribution to the overall polarization. In order to refine the mechanism for the generation of nonequilibrium nuclear polarization in the photolysis of cyclic ketones, we should analyze other magnetic and spin effects. One such effect is the magnetic isotope effect [4]. We were able to observe a change in the carbon-13 content at the carbonyl carbon and α-carbon in the photolysis of an aqueous solution of cyclohexanone with a natural isotope content [5].

In the present work, we studied the change in the relative carbon-13 content during the gas-phase photolysis of cyclohexanone and compared these data with the results for the photolysis of an aqueous solution.

EXPERIMENTAL

A commercial sample of cyclohexanone carefully purified by distillation was subjected to photolysis. The physicochemical indices of this sample were in accord with literature values. The photolysis was carried out in a 0.5-liter quartz flask using a DRSh-500 lamp and an aqueous light filter. The sample was heated to its boiling point in order to increase its

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