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SHORT COMMUNICATIONS

Synthesis and Transformations of γ-Chlorobutanoic Acid Phenyl(ethyl)amide

N. N. Yusubov, V. M. Ismailov, and Z. A. Mamedova

Baku State University, Baku, AZ-1148, Azerbajdzhan
e-mail: niftali-yusubov@rambler.ru

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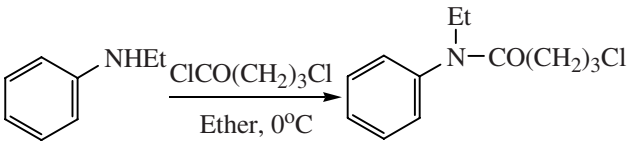
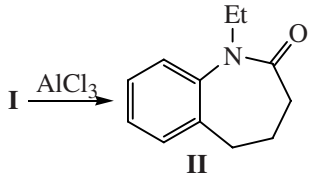
Trimethylenecarbonyl fragment is a structural base of many biologically active compounds [1, 2]. A convenient synthon for introducing this fragment is γ-chlorobutyryl chloride. It was previously established [3, 4] that alkoxybenzenes acylation with γ-chlorobutyryl chloride led to the formation of heterocyclic compounds.

In this study we investigated the acylation of *N*-ethylaniline with γ-chlorobutyryl chloride that proceeded with the formation of the corresponding N-acylated product, γ-chlorobutyric acid ethylphenylamide (**I**).



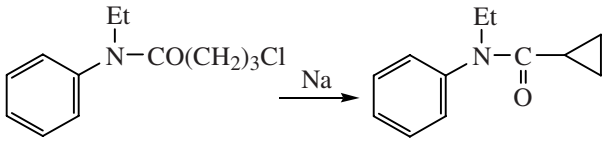
I

In the presence of alkaline and acidic catalysts amide **I** suffered a number of interesting transformations. The boiling of compound **I** in hexane in the presence of $AlCl_3$ resulted in intramolecular alkylation into the *ortho*-position of the aromatic ring giving a bicyclic compound 1-ethyl-2,3-benzazepin-7-one (**II**).



II

In the presence of sodium metal amide **I** is alkylated yielding a cyclopropane derivative, *N*-ethyl-*N*-phenylcyclopropylamide (**III**).



III

γ-Chlorobutyric acid *N*-ethyl-*N*-phenylamide (I). To 24.0 g (0.2 mol) of *N*-ethylaniline in 100 ml of ether at cooling (0°C) while stirring was gradually added 14.51 g (0.1 mol) of γ-chlorobutyryl chloride. The mixture was stirred for 2 h, then it was treated with water and extracted with ether. The ether extract was dried with Na_2SO_4, ether was distilled off, the residue was distilled in a vacuum. Yield 14 g (62%), bp 125°C (0.05 mm Hg), d_4^{20} 1.0990, n_D^{20} 1.5386. MR_D 64.21, calc. 64.24. ^1H NMR spectrum, δ, ppm: 1.0 t (3H, CH_3), 1.2 m (2H, CCH_2C), 1.97 m (2H, CH_2CO), 3.4 q (2H, NCH_2), 3.5 t (2H, CH_2Cl), 7.25 m (5H, C_6H_5). Found, %: Cl 15.52; N 6.08. $C_{12}H_{16}ClNO$. Calculated, %: Cl 15.74; N 6.20.

1-Ethyl-2,3-benzazepin-7-one (II). To 4.50 g (0.02 mol) of amide **I** in 50 ml of heptane at cooling while stirring was gradually added 7.98 g (0.06 mol) of $AlCl_3$. The mixture was heated for 2 h at 60–70°C. On cooling the mixture was poured on a mixture of 100 g of ice and 10 ml of concn. HCl, the reaction product was extracted into heptane, and the extract was dried over Na_2SO_4. Yield 1.0 g (26%), bp 135°C (0.03 mm Hg), d_4^{20} 1.0701, n_D^{20} 1.5428. MR_D 55.63, calc. 55.76. ^1H NMR spectrum, δ, ppm: 1.0 t and 3.5 q (5H, N–Et), 2.2 m (2H, CH_2Ph), 1.1 m (2H, CCH_2C), 2.6 m (CH_2CO), 6.8–7.0 m (4H,C_6H_5). Found, %: C 75.95; N 7.13. $C_{12}H_{15}NO$. Calculated, %: C 76.19; N 7.60.

***N*-Ethyl-*N*-phenylcyclopropylamide (III).** A mixture of finely dispersed sodium metal and 4.5 g (0.02 mol)

of initial amide **I**, was stirred in boiling toluene for 2 h. On cooling the separated sodium chloride was filtered off, toluene was distilled off, and the residue was distilled in a vacuum. Yield 1.8 g (48%), bp 112°C (0.05 mm Hg), d_4^{20} 1.0367, n_D^{20} 1.5294. MR_D 55.27, calc. 55.76. ^1H NMR spectrum, δ, ppm: 0.75–1.1 m (7H, CH_3 and CH_2CH_2), 2.2 m (1H, CH), 3.7 q (2H, NCH_2), 7.25 m (5H, C_6H_5). Found, %: C 76.11; N 7.40. $C_{12}H_{15}NO$. Calculated, %: C 76.19; N 7.60.

IR spectra were recorded on a spectrophotometer UR-20 from samples pelletized with KBr. ^1H NMR spectra were registered on a spectrometer Varian T-80 from solutions in CCl_4.

REFERENCES

1. Badilescu, J., *Tetrahedron*, 1970, vol. 26, p. 4207.
2. Kapelevich, V.M., *Usp. Khim*., 1979, vol. 48, p. 1273.
3. Ismailov, V.M., Gyul'akhmedov, L.M., Radvan, Shaban, and Yusubov, N.N., *Sb. nauchn. trudov* (Collection of Scientific Reports), Baku: Azerbaidzhan. Gos. Univ, 1989, p. 54.
4. Yusubov, N.N., Radvan, Shaban, Ismailov, V.M., and Dzhanibekov, N.F., *Izv. Russian Akad. Nauk, Ser. Khim.,* 1992, p. 1685.