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Synthesis and crystal structure of 1-ethyl-3-(phenyl)-1,2,3-triazolium perchlorate

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Abstract: The isolation of stable carbenes of the Arduengo **(la)** and Wanzlick **(2a)** type has prompted us to look for stable nitrenium ions of the related structural type 1-ethyl-3-(phenyl)-1,2,3-triazolium perchlorate (6^+). The title compound $C_{10}H_{14}Cl\ N_3O_4$ was isolated and structure was investigated by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 6.697(4)$ Å, $b = 9.724(9)$ Å, $c = 19.844(2)$ Å and $Z = 4$. The final residual factor is $R1 = 0.0471$ for 1545 reflections with $I > 2\sigma(I)$. The structure exhibits intermolecular hydrogen bonds.

Keywords: Nitrenium ions, Carbenes, Triazolium perchlorates, Crystal structure

1 Introduction

The chemistry of aromatic amines, amides have been receiving a lot of interest due to the carcinogenic activity and their synthetic utility [1]. The carcinogenic activities of all aromatic amines and amides are due to their metabolites like N-aryl hydroxy, N-aryl sulfoxy derivatives and nitrenium ions [2]. Nitrenium ions are involved as highly reactive intermediates in a wide variety of organic reactions [3]. For example, aromatic

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nitrenium ion (Fig. 1) with R_1= aryl, R_2=H or C(O), CH_3, or SO_3, are considered to be the ultimate carcinogens in carcinogenesis initiated by aromatic amines [4]. Nitrenium ions are isoeletronic with carbenes R_2C: containing a cationic [5] divalent nitrogen atom R_2N+ . Recent time resolved studies allowed the UV and IR spectra of some short-lived aryl nitrenium ions to be measured and provided important results on their structure and reactivity [6]. Although electronically deficient molecules of the types mentioned above are extremely short-lived, Arduengo [7a] and Wanzlick [7b] et al recently isolated and structurally characterized stable crystalline carbenes (Fig. 1) concomitantly. Stable crystals of nitrenium ions, more precisely, ion pair of nitrenium ions were synthesized and their X-ray crystal structures obtained [8]. From experimental data and theoretical calculations it emerged that these molecules are stabilized by electronic delocalization [9]. Intramolecular rearrangement reaction of nitrenium ions have been reported, and established as useful intermediates in wide variety of biological applications [10]. In our previous work, we described the synthesis of some stable nitrenium ions [8] and their comparison study with structurally related carbenes and found that stable nitrenium ions (as their carbene analogues) are electronically different from non stable ones. To get further insight into their exact nature and role of nitrenium ions, the title compound 6^+ was synthesized as per scheme 1 and characterized by proton and carbon NMR, elemental analyses and its structure is conformed by X-ray studies.

2 Experimental

2.1 Synthesis and Characterization

3-(2-Hydroxyethyl)-3-ethyl-1-(phenyl)-triazene (5):
5 was synthesized by diazotisation of aniline (9.31 gm, 100 mmol). Aniline was dissolved in 25 ml of 37% concentrated hydrochloric acid, 50 ml of water and cooled to 0 °C in ice bath and added sodium nitrite (7.6 gm, 110 mmol) to this cold solution. The diazonium salt solution **4** was mixed with a cold solution of 2-ethylamino-ethanol (9.80 gm, 110 mmol, in 20% Na_2CO_3). The mixture was stirred for 30 minutes at 0 °C, extracted with ether, washed with water, dried with $MgSO_4$, and the solvent was evaporated. The product was distilled under reduced pressure at 125-130°C to yield yellow oil (58%). mp: 10-12°C bp: 135-137 °C.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.45 (t, 3H, CH_3-CH_2), 3.36 (s, 1H, OH), 3.52 (q, 2H, CH_2-CH_3), 3.83-3.91 (m, 4H, CH_2-CH_2); 7.57 (s, 5H, Ar-H); ^{13}C NMR ($CDCl_3$, 100 MHz); δ(ppm): 28.3, 39.6, 48.8, 51.21, 117.3, 127.8, 129.6, 135.6; IR (Nujol); ν_{max} (cm^{-1}): 3435 (OH), 1622 (C=C), 1548 (C-N); (Ana. Cacld. for. $C_{10}H_{15}N_3O$: C, 62.17; H, 7.77; N, 21.76; Found: C, 62.32, H; 7.81; N, 21.63)

1-ethyl-3-(phenyl)-1,2,3-triazolium perchlorate (6^+):
To a solution of triazene **5** (0.177 gm, 10 mmol) and triethylamine (0.153 ml, 11.0 mmol) were added to 10 ml of dichloromethane at -15-10 °C. Added drop wise quickly a solution