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NEW REARRANGEMENT OF OXAZOLIUM SALTS INTO Δ^3-PYRROLIN-2-ONES

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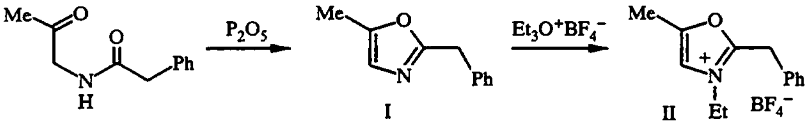
The possibility of recyclizing oxazolium salts into Δ^3-pyrrolin-2-ones by the action of base has been shown for the first time.

The recyclization of heterocyclic compounds initiated by the addition of nucleophile and ring fission has been known for a long time. Examples of this are the rearrangement of pyrilium salts [1] and the rearrangement of pyrones under the action of bases [2]. More than 35 years have elapsed since van der Plas first formulated the ANRORC mechanism [3, 4]. Tens of new reactions of aromatic and nonaromatic heterocyclic systems proceeding by this scheme have been discovered in that time. These include, for example, the rearrangement of pyridinium and pyrimidinium salts (the Kost–Sagitullin rearrangement [5, 6]) and of oxygen-containing heterocycles (4H-1,3-oxazinium salts [7]).

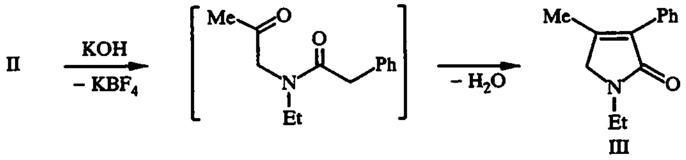
A common feature of these rearrangements is the fact that carbonyl-containing bifunctional compounds are formed as intermediates during the reaction and are capable of intramolecular cyclization with the formation of a C═C bond and not a C–N as in the case of the Dimroth rearrangement [8]. However, unlike the Dimroth rearrangement, rearrangements of this type have been studied mainly using six-membered heterocycles as examples [9].

We obtained 2-benzyl-3-ethyl-5-methyloxazolium tetrafluoroborate (II) by the interaction of oxazole (I) with triethyloxonium tetrafluoroborate according to [10], with the aim of studying the possibility of recyclizing five-membered heterocycles by an ANRORC mechanism, which includes the formation of a new C═C bond at the ring closure stage.



Heating compound (II) with an alcoholic solution of KOH leads to N-ethyl-4-methyl-3-phenyl-Δ^3-pyrrolin-2-one (III) in 70% yield.

The signal of the 4-H aromatic proton in the PMR spectrum of tetrafluoroborate (II) was observed as a singlet at 7.61 but the signals of the N–Et group protons were a quartet at 4.34 and a triplet at 1.47 ppm. An intense absorption band for C═O was observed at 1700 cm^{-1} in the IR spectrum of compound (III). The signals of the 5-H methylene protons in the PMR spectrum of compound (III) were observed as a singlet at 3.84, but the signals of the N-Et group were observed as a quartet at 3.52 and a triplet at 1.18 ppm. The ^{13}C NMR spectrum was in agreement with the structure of compound (III).



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We have shown it possible to recyclize oxazolium salts under the action of base, which is the first example of rearranging azoles like the known isomerization-recyclizations for six-membered nitrogen heterocycles.

EXPERIMENTAL

The PMR spectra were drawn on Bruker AC 200 P and Tesla BS-587-(80 MHz) instruments in $CDCl_3$. Internal standard was TMS. The IR spectra were recorded on a Specord IR-75 spectrometer in $CHCl_3$ solution. A check on the course of reactions and the purity of the compounds obtained was carried out by TLC on Silufol UV-254 plates, visualizing with iodine vapor and UV light.

2-Benzyl-5-methyloxazole (I). N-(2-Oxopropyl)phenylacetamide (0.50 g, 2.6 mmole) [11] was dissolved in absolute benzene and boiled with P_2O_5 (8 mmole) until disappearance of the starting material (check by TLC). The mixture was then neutralized with saturated Na_2CO_3 solution, extracted with benzene, and the solvent distilled off. 2-Benzyl-5-methyloxazole (0.37 g, 77%) was obtained of bp 117-120°C (8 mm Hg) [12]. IR spectrum: 1610, 1590, 1505 cm^{-1} (C=N, C=C).

N-Ethyl-2-benzyl-5-methyloxazolium Tetrafluoroborate (II). Triethyloxonium tetrafluoroborate (0.63 g, 3.3 mmole) in methylene chloride (10 ml) was added dropwise to a solution of 2-benzyl-5-methyloxazole (0.50 g, 2.9 mmole) in methylene chloride (15 ml). The reaction mixture was left overnight, the solvent then distilled off, and the residue triturated with absolute ether. The precipitated crystals were separated and N-ethyl-2-benzyl-5-methyloxazolium tetrafluoroborate (0.72 g, 86%) was obtained having mp 120-122°C (with decomposition). PMR spectrum: 7.61 (1H, s, 4-H); 7.42 (5H, s, Ph); 4.58 (2H, s, $-C\underline{H}_2-Ph$); 4.34 (2H, g, $J^3 = 7.2$ Hz, $-C\underline{H}_2-CH_3$); 2.49 (3H, s, $5-CH_3$); 1.47 ppm (3H, t, $J^3 = 7.2$ Hz, $-CH_2-C\underline{H}_3$). Found, %: C 54.33; H 5.87. $C_{13}H_{16}BF_4NO$. Calculated, %: C 54.01; H 5.58.

N-Ethyl-4-methyl-2-oxo-3-phenyl-Δ^3-pyrroline (III). Compound (II) (0.50 g, 1.7 mmole) was added to a solution of KOH (0.7 g) in ethanol (50 ml). The mixture was heated to boiling in a stream of inert gas, then cooled, and neutralized with 10% HC1. The solvent was distilled off and the residue extracted with benzene (2 × 15 ml). After distilling off the solvent the residue was purified by column chromatography on silica gel (eluent was $CHCl_3$−ethyl acetate, 2 : 1). Pyrrolinone (III) (0.278 g, 80%) was obtained of R_f 0.39 (liquid). IR spectrum: 1700 (CON), 1610 cm^{-1} (C=C). PMR spectrum: 7.39 (5H, m, Ph); 3.84 (2H, s, 5-H); 3.52 (2H, q, $J_3 = 7.3$ Hz, $-C\underline{H}_2-CH_3$); 2.10 (3H, s, $4-CH_3$); 1.18 ppm (3H, t, $J_3 = 7.3$ Hz, $-CH_2-\underline{C}\underline{H}_3$). ^{13}C NMR spectrum: 170.5 (C=O); 147.4 and 132.5 (C=C); 132.0, 128.8, 127.8, 126.9 (Ph); 53.7 ($C_{(5)}$); 36.8 ($N\underline{C}H_2CH_3$); 14.0 and 13.7 ppm ($4-CH_3$, $NCH_2\underline{C}H_3$). Found, %: C 77.48; H 7.67. $C_{13}H_{15}NO$. Calculated, %: C 77.58; H 7.51.

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