2-ETHYNYL-SUBSTITUTED IMIDAZOLES

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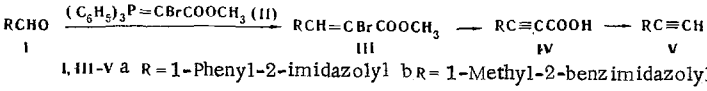
UDC 547.785.5:547.39:547.314.2

2-Ethynyl-substituted imidazoles have been unknown up to now. We have synthesized 2-ethynyl derivatives of imidazole and benzimidazole by means of the Wittig reaction. The reaction of 2-formyl derivatives of 1-phenylimidazole (Ia) [1] and 1-methylbenzimidazole (Ib) [2] with carbomethoxybromomethylenetriphenylphosphorane (II) [3] gave esters of substituted α-bromoacrylic acids (III), which were converted to 1-phenyl-2-imidazolyl- and 1-methyl-2-benzimidazolylpropiolic acids with alcoholic alkali; the latter are readily decarboxylated to give imidazolylacetylenes due to the effect of the heteroaromatic ring.



I, III-V a R = 1-Phenyl-2-imidazolyl b R = 1-Methyl-2-benzimidazolyl

EXPERIMENTAL

Methyl α-Bromo-β-(1-phenyl-2-imidazolyl)acrylate (III). Ia [0.86 g (5 mmole)] and 2.1 g (5 mmole) of II were refluxed in 15 ml of benzene for 8 h to give 0.8 g (53%) of a product with mp 165° (colorless prisms from ethyl acetate). Found %: C 51.2; H 3.8; Br 25.8; N 9.5. $C_{13}H_{11}BrN_2O_2$. Calc. %: C 50.9; H 3.7; Br 26.0; N 9.1.

Methyl α-Bromo-β-(1-methyl-2-benzimidazolyl)acrylate (IIIb). This was obtained in 68% yield and had mp 186° (colorless prisms from benzene). Found %: C 49.9; H 4.2; Br 26.8; N 9.5. $C_{12}H_{11}BrN_2O_2$. Calc. %: C 48.9; H 3.8; Br 27.1; N 9.5.

1-Phenyl-2-imidazolylpropiolic Acid (IVa). This compound was obtained in 79% yield and had mp 101-102°. Found %: N 13.0. $C_{12}H_8N_2O_2$. Calc. %: N 13.2. IR spectrum (in mineral oil, UR-20 spectrometer): 1712 cm^{-1} (CO), 2225 cm^{-1} (C ≡ C).

1-Methyl-2-benzimidazolylpropiolic Acid (IVb). This compound was obtained in 71% yield and had mp 84°. Found %: N 14.2. $C_{11}H_8N_2O_2$. Calc. %: N 14.0. The IR spectrum of the potassium salt contained a band at 2220 cm^{-1} (C ≡ C).

1-Phenyl-2-ethynylimidazole (Va). A water suspension of IVa was heated on a water bath for 30 min, and the resulting oil was extracted with chloroform and chromatographed on aluminum oxide to give 36% of a product with mp 60° (colorless prisms from petroleum ether). Found %: C 78.2; H 5.0; N 16.7. $C_{11}H_8N_2$. Calc. %: C 78.5; H 4.8; N 16.6. IR spectrum: 2130 cm^{-1} (C ≡ C) and 3310 cm^{-1} (≡ C – H, $CHCl_3$). A silver acetylide was prepared from Va. Found %: Ag 39.7. $C_{11}H_7AgN_2$. Calc. %: Ag 39.2.

1-Methyl-2-ethynylbenzimidazole (Vb). This compound was similarly obtained in 38% yield and had mp 100° (colorless prisms from petroleum ether). Found %: C 76.6; H 5.3; N 18.0. $C_{10}H_8N_2$. Calc. %: C 76.9; H 5.2; N 17.9. IR spectrum: 2115 cm^{-1} (C ≡ C), 3190 cm^{-1} (≡ C – H). A silver acetylide was prepared from Vb. Found %: Ag 40.6. $C_{10}H_7AgN_2$. Calc. %: Ag 41.0.

Rostov-on-Don State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 139-140, January, 1971. Original article submitted December 30, 1969.

LITERATURE CITED

1. A. M. Simonov and L. M. Sitkina, Khim. Geterotsikl. Soedin., No. 1, 116 (1967).
2. M. T. LeBris and H. Wahl, Bull. Soc. Chim. France, 343 (1959).
3. G. Märkl, Ber., 94, 2996 (1961).