REACTION OF SOME 3,4-DINITROPYRAZOLINES WITH BASES

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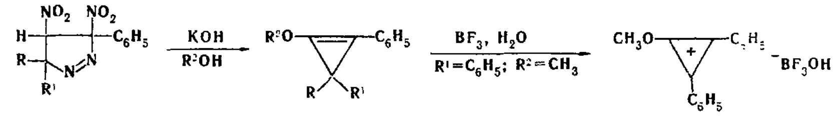
It is known [1] that mononitropyrazolines are converted to pyrazoles under the influence of bases. We have observed that 3,5,5-triphenyl-3,4-dinitropyrazoline (I), with mp 95° (dec.), and 3-phenyl-5-diphenylyl-3,4-dinitropyrazoline (II), with mp 86° (dec.), obtained by reaction of diphenyldiazomethane and 9-diazofluorene with 1-phenyl-1,2-dinitroethylene by the method in [2] in 84 and 74% yields, respectively, decompose in an alcoholic alkali solution at 20-25°C with splitting out of nitrogen and both nitro groups to give 1,1,2-triphenyl- and 1-diphenylyl-2-phenyl-3-alkoxycyclopropenes (III-VI). The reaction is accompanied by intense gas evolution. The cyclopropenes were recrystallized from methanol: III, mp 117-118°; IV, mp 108-109°; V, mp 134-135°; VI, mp 69-70°. The products were obtained in 98, 97, 88, and 75% yields, respectively.

This reaction is due to the presence of a labile hydrogen atom in the 4 position of the pyrazoline ring and of two nitro groups. 4-Substituted 3,4-dinitropyrazolines (for example, 3,4,5-triphenyl-3,4-dinitropyrazoline [2]) do not react with bases.



I, II III-VI VII

III $R=R^1=C_6H_5$, $R^2=CH_3$; IV R and R^1=diphenylyl, $R^2=CH_3$; V R and R^1=diphenylyl, $R^2=C_2H_5$; VI $R=R^1=C_6H_5$, $R^2=C_2H_5$

The IR spectra of III-VI contain absorption bands of a C=C bond (1912-1938 cm^{-1}) and of a C—O—C bond (1256-1265 cm^{-1}), whereas the spectra of III and IV also contain the absorption band of a CH_3O group (2840 cm^{-1}). Compound III undergoes the characteristic (for cyclopropenes) reaction with boron trifluoride etherate in the presence of water to give the cyclopropenylium cation (VII).

The IR spectrum of VII contains the frequency of the vibrations of an OH group (3230 cm^{-1} and of the cyclopropenylium cation (1460 cm^{-1}).

All of the synthesized compounds were identified from the results of elementary analysis and the IR and PMR spectra.

LITERATURE CITED

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2. F. A. Gabitov, A. L. Fridman, and O. B. Kremleva, Khim. Geterotsikl. Soedin., No. 11, 1577 (1975).

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