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Abstract

Full Text

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V. N. CHISTOKLETOV, A. T. TROSHCHENKO, and A. A. PETROV

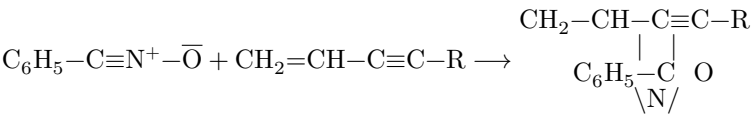
INTERACTION OF VINYLACETYLENE AND ITS HOMOLOGS WITH BENZONITRILE OXIDE

(Presented by Academician B. A. Arbuzov, June 20, 1960)

It was shown earlier that vinylacetylene adds diazomethane selectively, at the double bond, with formation of 3-ethynylpyrazoline (⁀1). Nitrile oxides are analogous in structure to diazoparaffins and are also capable, at ordinary temperature, of adding to multiple bonds of ethylenic and acetylenic hydrocarbons with formation, respectively, of isoxazolines (⁀2) and isoxazoles (⁀3). Reactions with dienes may proceed with participation of one or both double bonds (⁀4). In the case of fulvenes, the semicyclic double bond at the tertiary carbon is inactive. Divinylacetylene gives, with benzonitrile oxide, 5,5′-ethylene-bis-3-phenyl-2-isoxazoline in almost quantitative yield (⁀4). Data on the order of addition of benzonitrile oxide to vinylacetylene and its homologs are absent from the literature.

We set ourselves the task of establishing the order of addition of benzonitrile oxide to enyne hydrocarbons and of determining the possibility of obtaining, in this way, crystalline derivatives convenient for identification of the named hydrocarbons.

The experiments carried out showed that benzonitrile oxide readily adds to vinylacetylene, vinylmethylacetylene, and vinylethylacetylene exclusively at the double bond, with formation, respectively, of 3-phenyl-5-ethynyl-2-isoxazoline (I), 3-phenyl-5-methylethynyl-2-isoxazoline (II), and 3-phenyl-5-ethylethynyl-2-isoxazoline (III), according to the scheme:



where $R = H$ (I), CH_3–(II), or C_2H_5–(III).

The structure of the substances obtained was established by several methods. In the infrared spectra of all three condensation products there were absorption bands characteristic of the acetylenic grouping (2120 and 3310 cm^{-1} in the case

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Fig. 1. Infrared transmission spectra: 1—3-phenyl-5-ethynyl-2-isoxazoline, 2—3-phenyl-5-methylethynyl-2-isoxazoline, 3—3-phenyl-5-ethylethynyl-2-isoxazoline

Figure 1: Fig. 1. Infrared transmission spectra: 1—3-phenyl-5-ethynyl-2-isoxazoline, 2—3-phenyl-5-methylethynyl-2-isoxazoline, 3—3-phenyl-5-ethylethynyl-2-isoxazoline

of substance (I), and about 2240 cm^{-1} in the case of substances (II) and (III)). Absorption bands characteristic of the vinyl group (in the region 900–1000 cm^{-1}) were absent from the spectra (Fig. 1). In the product of addition of benzonitrile oxide to vinylacetylene (I), 99.5–99.8% of a substance with a terminal acetylenic grouping was found by the mercury method (ˆ5).

Upon oxidation of the products of addition of benzonitrile oxide to vinyl-, vinylmethyl-, and vinylethylacetylenes with an alkaline solution of potassium permanganate, in all cases one and the same 3-phenyl-2-isoxazoline-5-carboxylic acid, described in the literature, was obtained; it was identified by the melting points of mixed samples of the acid itself and of its anilide. In the case of addition of benzonitrile oxide to the hydrocarbons investigated ···

upon oxidation at the triple bond, three different isoxazolecarboxylic acids should have been formed: 3-phenylisoxazole-5-carboxylic, 3-phenyl-4-methylisoxazole-5-carboxylic, and 3-phenyl-4-ethylisoxazole-5-carboxylic acids.

Apparently, benzonitrile oxide, like diazomethane ([1]), adds to the double bond of enyne hydrocarbons as a nucleophilic reagent. Enyne hydrocarbons react in the same way with lithium alkyls, lithium amides, and lithium phosphides ([6]). All three isoxazolines obtained proved to be crystalline substances convenient for identifying the initial enyne hydrocarbons.

Fig. 1. Infrared transmission spectra: 1—3-phenyl-5-ethynyl-2-isoxazoline, 2—3-phenyl-5-methylethynyl-2-isoxazoline, 3—3-phenyl-5-ethylethynyl-2-isoxazoline

The reaction of enyne hydrocarbons with nitrile oxides may also serve as a convenient method for obtaining isoxazolines with acetylenic radicals.

Experimental Part

3-Phenyl-5-ethynyl-2-isoxazoline (I). A solution of 0.4 g-mol of freshly distilled vinylacetylene in 150 ml of anhydrous ether was mixed at −15° with an ethereal solution (200 ml) of benzonitrile oxide, obtained from 0.1 g-mol of benzohydroxamic acid chloride ([2],[3]). The mixture was left to stand in a closed thick-walled bottle at room temperature for 24 hours. After removal of the ether under reduced pressure, the remaining yellow oil crystallized after 6 hours. Yield of crude product 7 g (41% based on benzonitrile oxide).

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On recrystallization from methanol, a small amount of diphenylfuroxan was separated, and from the mother liquor 3-phenyl-5-ethynyl-2-isoxazoline was obtained. Colorless needle-like crystals, m.p. 69-70° (from carbon tetrachloride).

Found, %: C 77.03; 77.09; H 5.42; 5.46; N 8.16; 8.20
$C_{11}H_9NO$. Calculated, %: C 77.17; H 5.29; N 8.18

IR spectrum (5% solution in CCl_4)*: 848 w, 895 v.s., 1004 m, 1040 m,

* Very weak frequencies are not given.

1075 w, 1162 m, 1231 w, 1277 m, 1328 s, 1358 v.s., 1437 m, 1450 s, 1498 w, 1564 w, 1600 m, 2120 w, 2850 w, 2927 m, 3032 m, 3061 m, 3103 w, 3310 v.s. cm^{-1}.

To a solution of 0.5 g of 3-phenyl-5-ethynyl-2-isoxazoline in 20 ml of acetone, 0.6 g of powdered potassium permanganate was gradually added. Slight warming was observed. The acetone was distilled off and the residue was treated with water. The filtrate from manganese dioxide was acidified with 10% H_2SO_4. The crystalline precipitate that separated was recrystallized from water. M.p. 143-144°. The anilide of the acid, obtained in the usual way with thionyl chloride, had m.p. 155-156°.

Literature data: 3-phenyl-2-isoxazoline-5-carboxylic acid, m.p. 143-144°; anilide, m.p. 155-156° ([2]).

3-Phenyl-5-methylethynyl-2-isoxazoline (II). A solution of 0.075 g-mole of vinylmethylacetylene in 100 ml of ether was mixed with a solution of benzonitrile oxide (from 0.15 g-mole of benzhydroxamic acid chloride) in 300 ml of dry ether. After standing at room temperature for 24 h, the ether was distilled off under reduced pressure until precipitation began. Fifteen grams of crude 3-phenyl-5-methylethynyl-2-isoxazoline were filtered off. From the mother liquor, 6 g of diphenylfuroxan was obtained.

After recrystallization from methanol and then from carbon tetrachloride, isoxazoline (II) had a constant m.p. of 99-100°. Yield 95% (based on vinylmethylacetylene).

Found %:	C 78.29; 77.81;	H 6.15; 6.36;	N 7.81; 7.65
$C_{12}H_{11}NO$. Calculated %:	C 77.86;	H 5.98;	N 7.56

IR spectrum (5% solution in CCl_4): 838 s, 898 v.s., 1020 w, 1178 m, 1236 w, 1330 s, 1357 v.s., 1451 s, 1500 w, 1570 w, 1600 m, 2245 m, 2855 w, 2923 s, 3034 m, 3045 m, 3063 m, 3108 w cm^{-1}.

Upon oxidation of isoxazoline (II) under the conditions described above, 3-phenyl-2-isoxazoline-5-carboxylic acid was obtained, having m.p. 143-144° and anilide m.p. 155-156°. Mixed samples of the acid and its anilide with the preparations described earlier showed no depression.

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3-Phenyl-5-ethylethynyl-2-isoxazoline (III). From 0.07 g-mole of vinylethylacetylene and nitrile oxide, obtained from 0.078 g-mole of benzhydroxamic acid chloride, 10 g (75% based on vinylethylacetylene) of 3-phenyl-5-ethylethynyl-2-isoxazoline was obtained.

M.p. 64-65° (from aqueous methanol and then from ligroin). Colorless needle crystals.

Found %:	C 78.68; 78.37;	H 6.86; 6.81;	N 7.62; 7.56
$C_{13}H_{13}NO$. Calculated %:	C 78.36;	H 6.59;	N 7.03;

IR spectrum (5% solution in CCl_4): 840 s, 891 s, 977 w, 1161 w, 1169 w, 1231 w, 1322 s, 1353 s, 1443 s, 1468 m, 1495 m, 1592 s, 2242 w, 2848 w, 2881 m, 2926 w, 2938 m, 2978 s, 3027 w, 3061 m cm^{-1}.

Oxidation, carried out as in the preceding cases, gave 3-phenyl-2-isoxazoline-5-carboxylic acid. M.p. 143-144°. Anilide, m.p. 155-156°. Mixed samples with authentic preparations showed no depression of the melting point.

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