CYCLIZATION OF 4,4-DINITROBUTENOIC ACID ESTERS TO 3-NITROISOXAZOLINE N-OXIDES

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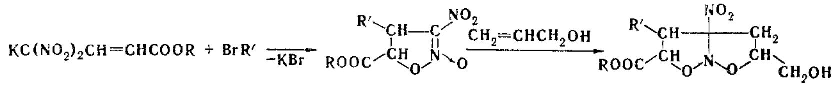
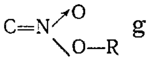
It is known that salts of nitroalkanes are readily halogenated by N-halo derivatives of amides, imides, and nitroamines. We have observed that the reaction of the potassium salts of 4,4-dinitrobutenoic acid esters (I) with the N-bromo derivatives of succinimide and N-methyl-p-toluenesulfonamide is accompanied by cyclization to 4,5-substituted 3-nitroisoxazoline N-oxides (IIa-e).



I IIa-e III

IIa-d $R' = (-CH_2CO)_2N$; a, e $R = CH_3$; b $R = C_2H_5$; c $R = n\text{-}C_3H_7$; d $R = (C_6H_5)_2CH$; e $R' = p\text{-Tos-N-CH}_3$

Compounds IIa-e display properties characteristics for 3-nitroisoxazoline N-oxides. They slowly liberate iodine from KI in acetic acid and undergo 1,3-dipolar cycloaddition with olefins to give nitroisoxazolizidines (III). Absorption bands of the C = N bond (1650-1665 cm^{-1}), of a nitro group (1516-1522 and 1320-1330 cm^{-1}), and of a  $C{=}N{\overset{\nearrow O}{\underset{\searrow O-R}{}}}$ grouping (812-820 and 1220-1240 cm^{-1}) are observed in the IR spectra of IIa-e. A hypsochromic shift of the absorption band at 300-310 nm as compared with the spectra of unsubstituted 3-nitroisoxazoline N-oxides (λ_{max}, CH_2Cl_2 320 nm) is observed in the UV spectra. The strucure and individuality of IIa-e are also confirmed by the results of elementary analysis and thin-layer chromatography [Silufol, acetone–chloroform (1 : 8)].

3-Nitroisoxazoline N-Oxides (IIa-e). A solution of 20 mmole of N-bromo derivative in 20-30 ml of acetone was added at 20-25° to a solution of 20 mmole of salt I in 15-20 ml of acetone, and the mixture was held at this temperature for 0.5-1 h. It was then filtered, and the filtrate was evaporated. The residue was recrystallized from ethanol. Compound IIa, with mp 208-209° (dec.) and R_f 0.35, was obtained in 86% yield. IR spectrum: 1740, 1720, 1650, 1520, 1325, 1220, and 812 cm^{-1}. UV spectrum: λ_{max} 306 nm (log ε 4.01). Compound IIb, with mp 186-187° (dec.) and R_f 0.45, was obtained in 68% yield. IR spectrum: 1755, 1720, 1660, 1512, 1320, 1240, 820 cm^{-1}. UV spectrum: λ_{max} 308 nm (log ε 4.01). Compound IIc, with mp 192-193° (dec.) and R_f 0.68, was obtained in 65% yield. IR spectrum: 1765, 1725, 1670, 1520, 1330, 1218, and 820 cm^{-1}. UV spectrum: λ_{max} 305 nm (log ε 4.01). Compound IId, with mp 211-212° (dec.) and R_f 0.30, was obtained in 61% yield. IR spectrum: 1770, 1745, 1665, 1520, 1330, 1225, 820 cm^{-1}. UV spectrum: λ_{max} 307 nm (log ε 4.08). Compound IIe, with mp 174-175° (dec.) and R_f 0.80, was obtained in 84% yield. IR spectrum: 1755, 1650, 1515, 1320, 1235, 1178, and 813 cm^{-1}. UV spectrum: λ_{max} 299 nm (log ε 3.85).

Reaction of Isoxazoline IIa with Allyl Alcohol. Allyl alcohol (30 ml) was added at 60-70° to a solution of 1 g of IIa in 80 ml of acetonitrile, after which the mixture was held at this temperature for 1 h. It was then evaporated, and the residue was recrystallized from ethanol to give IIIa with mp 170-171° (dec.) in 80% yield. IR spectrum: 3540, 1735, 1568, 1380, 1310, 1185, and 820 cm^{-1}. Found: C 42.1; H 4.5; N 12.4%. $C_{12}H_{15}N_3O_9$. Calculated: C 41.7; H 4.3; N 12.2%.

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