## Nov. 1977 Reaction of Vinyl Ketoximes with N-Bromosuccinimide. Synthesis of Isoxazoles and 4-Bromoisoxazolines.

John F. Hansen (1) and Scott A. Strong

Department of Chemistry, Illinois State University, Normal, Illinois 61761 Received August 22, 1977

The reaction of some selected  $\alpha,\beta$ -unsaturated oximes with N-bromosuccinimide gave isoxazoles or 4-bromoisoxazolines in moderate to good yields.

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Sir:

The reaction of  $\alpha,\beta$ -unsaturated oximes with iodine-potassium iodide has been reported by Büchi and Vederas as a method for the synthesis of isoxazoles (2). However, these authors report that efforts to replace iodine with donors of positive chlorine or bromine failed without exception. We now wish to report the results of our preliminary investigation into the reaction of a series of  $\alpha,\beta$ -unsaturated oximes 1a-d with N-bromosuccinimide (NBS) to give isoxazoles or 4-bromoisoxazolines in good yield.

In our initial studies a solution of 40 mmoles of 1a in 150 ml. of benzene was treated at room temperature over fifteen minutes with 44 mmoles of NBS. After one hour the mixture was filtered, and the filtrate was applied to a column of 150 g. of alumina and rapidly eluted with benzene. The first 300 ml. of eluent was collected and evaporated to yield 64% of 4-bromo-3,5-diphenylisoxazoline 2, m.p. 152-153° (reported m.p. 152-153°) (3). Further evidence for the structure of 2 was obtained by dehydrohalogenation with methanolic potassium hydroxide to give 3,5-diphenylisoxazole.

The reaction of 1,2,3-triphenyl-2-propen-1-one oxime 1b with NBS under the above conditions did not lead to the isolation of a 4-bromoisoxazoline. In this case the product, isolated in 82% yield, was 3,4,5-triphenylisoxazole 3, m.p. 211-212° (reported m.p. 212°) (4). It seems likely that a 4-bromoisoxazoline intermediate is formed, but that dehydrohalogenation to 3 occurs under the reaction conditions or during workup. Similar behavior is observed for 1c, which gives 57% of 4-bromo-3,5-diphenylisoxazole 4, m.p. 132-134° (reported m.p. 132.5-133.5°) (5).

A further structural variation examined is represented by 1,3,3-triphenyl-2-propen-1-one oxime 1d. In this instance 4-bromo-3,5,5-triphenylisoxazoline 5, m.p. 189-191°, was obtained in 55% yield. The structure of 5 was assigned on the basis of its elemental analysis (Calcd. for C<sub>21</sub>H<sub>16</sub>BrNO: C, 66.66; H, 4.29; N, 3.70. Found: C, 66.99; H, 4.51; N, 3.67) and its pmr spectrum (δ, deuteriochloroform) which included a complex multiplet for the 15 protons on the phenyl substituents and a

singlet at 6.02 for the proton at C-4. Further evidence for the structure of 5 was obtained from its reaction with ethanolic silver nitrate. Upon warming for 15 minutes, a precipitate corresponding to approximately one equivalent of silver bromide was obtained. Interestingly, the organic product formed from the reaction with silver nitrate was identical with 3 formed above. The formation of 3 from 5 may be explained as the result of the migration of a phenyl group from C-5 to C-4 in a typical carbonium ion-type rearrangement.

The above preliminary study suggests that the reaction of  $\alpha,\beta$ -unsaturated oximes with NBS may provide a convenient route to isoxazoles and 4-bromoisoxazolines. We are pursuing further investigations in the scope of this reaction and in the interesting rearrangement reaction of 4-bromoisoxazolines.

## REFERENCES AND NOTES

- (1) Author to whom correspondence should be addressed.
- (2) G. Büchi and J. C. Vederas, J. Am. Chem. Soc., 94, 9128 (1972).
- (3) G. S. D'Alcontres and P. Grünanger, Gazz. Chim. Ital., 80, 831 (1950).
  - (4) F. Heim, Ber., 44, 2016 (1911).
- (5) N. K. Kochetkov, S. D. Sokolov, and N. M. Vagurtova, Zhur. Obshch. Khim., 31, 2326 (1961).