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CYCLODIMERIZATION OF 3-METHYL-3-BUTEN-2-ONE OXIME*

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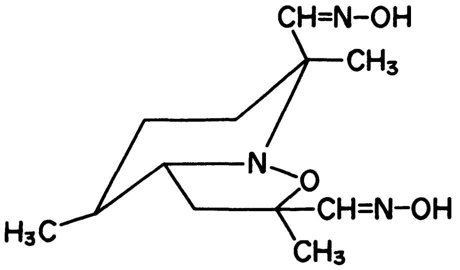
Nitron derivative, 8-hydroxy-1,4,5,7-tetramethyl-6,8-diazabicyclo [3.2.1]oct-6-ene 6-oxide, was obtained by the cyclodimerization of 3-methyl-3-buten-2-one oxime at 80 °C. This nitron was easily converted into the stable nitroxy radical by the attack of poly(N-methylacrylamide) radical.

Cyclodimerization of heteroatom substituted 1,3-dienes such as acrylaldehydes,[1)] 3-buten-2-ones,[2,3)] and 3-buten-2-thiones[4)] has been interested by many authors in connection with the Woodward-Hoffmann rules and with the initiation mechanism of spontaneous thermal polymerizations. However, such a reaction of nitrogen substituted 1,3-dienes has been little known. In the preceding paper,[5)] we found that methacrylaldehyde oxime was easily converted into the trimer (1) by the heating at 80 °C. Unfortunately, attempts to isolate the desired intermediate, the cyclic dimer, were unsuccessful. In the course of the study on the polymerization of 3-methyl-3-buten-2-one oxime (MIKOM), we noticed that MIKOM was converted preferentially into the cyclic dimer. In this note, we wish to report on the cyclodimerization of MIKOM and also on the reaction of the MIKOM dimer with radical species.



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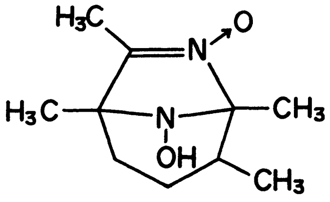

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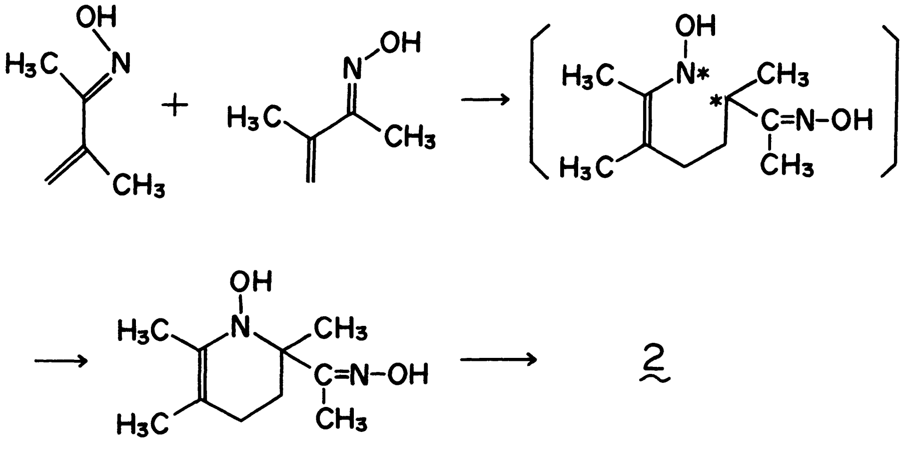
Heating of MIKOM, which was prepared by the reaction of 3-methyl-3-buten-2-one[6)] with hydroxylamine hydrochloride, at 80 °C in a degassed ampoule for 375 hours resulted in yellow solution. Unreacted MIKOM was removed by the distillation under reduced pressure, and then the residue was treated with large amount of ether to precipitate the dimer. Yield 12 %. MS (70 eV) m/e (relative intensity): 198 (M^+, 31), 181 (11), and 124 (100). IR (KBr): 3150 (OH) and 1601 cm^{-1} (C=N). Found: C, 60.85; H, 9.33; N, 14.42 %. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.12 %.

To confirm the molecular structure of the dimer, the X-ray crystal structure analysis was carried out. The crystals of the dimer suitable for X-ray study were obtained by slow crystallization from its methanol solution, and then they were mounted on a Syntex R_3 automated four-circle diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71069 Å) The crystal was monoclinic with the space group $P2_1/n$ and identified as 8-hydroxy-1,4,5,7-tetramethyl-6,8-diazabicyclo[3.2.1]oct-6-ene 6-oxide (2). As can be expected from the structure, ^{13}C-NMR spectrum of 2 shows three singlet (δ = 71.88, 98.97, and 142.88 ppm), one doublet (δ = 36.51 ppm), two triplet (δ = 27.73 and 32.70 ppm), and four qualtet peaks (δ = 9.24, 14.06, 16.02, and 18.95 ppm). The resonances due to two methylene carbons are shifted to rather high fields, indicating the ring structure.

The process 3 → 2 may be very fast because no Diels-Alder adduct (3) was isolated. Therefore, dimerization reaction may be the rate-determining step, and two mechanisms are considered for this process, *i.e.*, one-step concerted two-stage and two-step unconcerted zwitterion mechanisms. According to the concerted



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mechanism which was proposed by Woodward and Katz$^{1)}$ for the cyclodimerizations of acrylaldehydes and substituted butadienes, two new bonds are formed simultanesouly even though there is a considerable asymmetry in the rate. The possibility of one-step and symmetry mechanism or of unconcerted biradical mechanism is less probable because of both asymmetrical and polar addenda. Although more predominant mechanism of the two is still not elucidated, it is clear that the reaction, as well as the dimerization of 3-buten-2-ones,$^{2)}$ proceeds with resioselectivity since other cyclic isomers were little detected.

In differential thermal analysis, the dimer has two peaks, an endothermic and an exothermic ones with the maxima at 164 and 232 °C, respectively. In dynamic thermogravimetric analysis, the weight loss was observed to begin at the melting point of 147 °C. These results support that this nitron is thermally stable.

The dimer showed high chemical reactivities, especially for the attack of radical species. For example, the rate of the radical polymerization of styrene in the presence of the dimer 1.8×10^{-2} mol/l was reduced to 70 % its original value. To study this subject in further detail, the reaction of the dimer with a propagating radical of poly(N-methylacrylamide) was followed by ESR measurements according to the previous technique.$^{7)}$ Figure 1 shows the ESR spectrum after the reaction for 5 days at a room temperature. Triplet with splitting constant a_N 14 gauss and g-value 2.0055 is observed, indicating the formation of the following nitroxy radical.

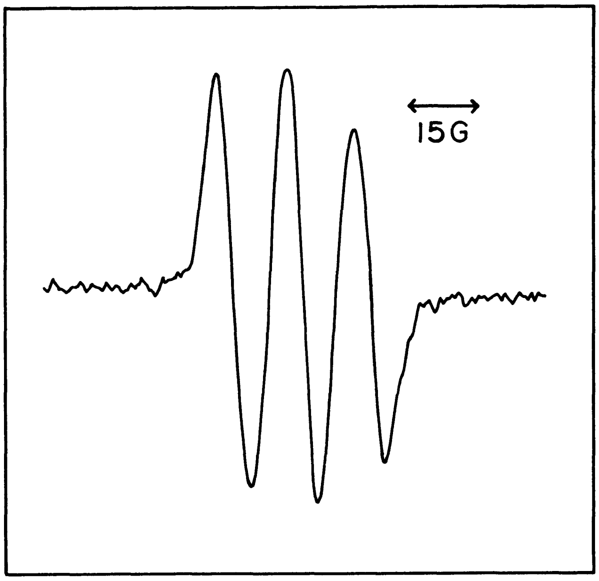
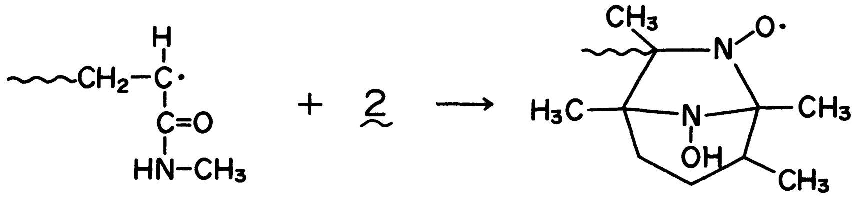


Fig. 1. ESR spectrum of the MIKOM dimer in chloroform at a room temperature



In the polymerization of styrene in the presence of the MIKOM dimer, it seems reasonable to assume that the production of such a stable nitroxy radical affects the rate of its polymerization.

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* Studies on the Polymerization of Acrolein Oxime. XV.

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