

Figure 1.—Left and right eye views of a hydroxypelenolide *p*-bromobenzoate molecule. Bond distances and their standard deviations in angstroms are given on the left eye view, and bond angles on the right eye view.

striking feature of this opening is the angle between the planes formed by C-2-C-1-C-10 and C-1-C-10-C-9, which would be very close to 0° in a simple alkene but is in this case 20°.

**Registry No.**—IIa, 17909-94-3; IIb, 25975-82-0; III, 17909-92-1.

**Acknowledgments.**—We thank the Oak Ridge National Laboratory for programs, S. H. Jay for assistance with programming, the University of Arizona Computer Center for computer time, and the PHS (GM-12447), the NSF (postdoctoral support for C. J. C., URP support for T. C. S.), and the Sloan Foundation (Fellowship to R. B. B.) for financial assistance.

## Notes

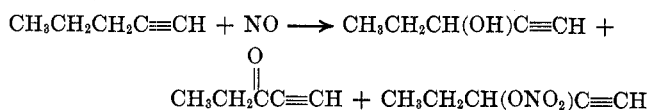
### Reaction of Nitric Oxide with 1-Pentyne

SAMUEL F. REED, JR.

*Rohm and Haas Company,  
Redstone Research Laboratories,  
Huntsville, Alabama 35807*

Received March 5, 1970

In contrast to reactions involving the addition of tetrafluorohydrazine to olefins in the presence of nitric oxide which gave predominately difluoramine-*N'*-fluorodiimide *N*-oxides,<sup>1</sup> we have found that with acetylenic compounds the reaction takes an alternate course to give in low-yield products devoid of carbon-nitrogen bonding. It was further established that tetrafluorohydrazine does not enter into the transformation, nor was it necessary for the interaction of nitric oxide with 1-pentyne. In the reaction with 1-pentyne, the products obtained were 1-pentyn-3-ol, 1-pentyn-3-one, and 1-pentyn-3-nitrate.



These reactions were conducted in an evacuated system at ambient temperature by first introducing 1-pentyne with or without solvent ( $\text{HCCl}_3$ ) into a reaction flask which was attached to a glass vacuum system and deaerated by alternate freeze-thaw cycles. The system was then charged with nitric oxide to 500–600 mm of pressure, and the mixture was warmed to reaction temperature for periods of 20–24 hr. Visibly, there was little indication of any reaction except for a

slight decrease in pressure. In all instances, 15–55% of the nitric oxide reacted with the formation of nitrogen, and 1-pentyne was converted to products in low conversions followed by termination of the reaction. This behavior was common to both lighted and covered reaction flask.

Gas chromatography was employed to analyze the product mixtures which showed the presence of three products separated in sufficient quantities on a preparative column for proton nmr spectral analysis. 1-Pentyn-3-ol displayed a triplet ( $J = 7$  cps) centered at  $\tau$  9.01 ( $\text{CH}_3$ ), a quintet ( $J = 7$  cps) at  $\tau$  8.20 ( $\text{CH}_2$ ), a doublet ( $J = 2$  cps) at  $\tau$  7.63 ( $\text{HC}\equiv$ ), a triplet ( $J = 7$  cps) of doublets at  $\tau$  5.74 ( $\text{HC}-\text{O}$ ), and a singlet at  $\tau$  6.46 ( $\text{OH}$ ). A triplet ( $J = 7$  cps) at  $\tau$  8.88 ( $\text{CH}_3$ ), a quadruplet ( $J = 7$  cps) at  $\tau$  7.43 ( $\text{CH}_2$ ), and a singlet at  $\tau$  6.80 ( $\text{HC}\equiv$ ) were exhibited in the spectrum of 1-pentyn-3-one. The nitrate ester of 1-pentyn-3-ol show absorption as a triplet ( $J = 7$  cps) at  $\tau$  8.90 ( $\text{CH}_3$ ), a quintet ( $J = 7$  cps) at  $\tau$  8.11 ( $\text{CH}_2$ ), a doublet ( $J = 2$  cps) at  $\tau$  7.48 ( $\text{HC}\equiv$ ), and a triplet ( $J = 7$  cps) of doublets ( $J = 2$  cps) at  $\tau$  4.68 ( $\text{HC}-\text{O}$ ). All peak areas were in the appropriate ratio, and the spectra and glc retention times were identical with those of authentic samples of the three compounds.

Treatment of 1-pentyn-3-ol with nitric oxide under the same conditions gave the ketone and nitrate ester in low yields, and again, the reaction stopped at low conversions. Similarly, when 1-hexyne was treated with nitric oxide the corresponding alcohol, ketone and nitrate ester were formed with low conversion of 1-hexyne to products.

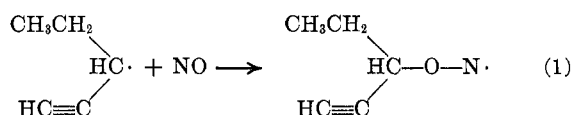
The preliminary results point to a free-radical process; however, nitric oxide while known<sup>2</sup> to be very efficient at trapping hydrocarbon radicals is not par-

(1) S. F. Reed, Jr., *J. Org. Chem.* **32**, 3869 (1967).

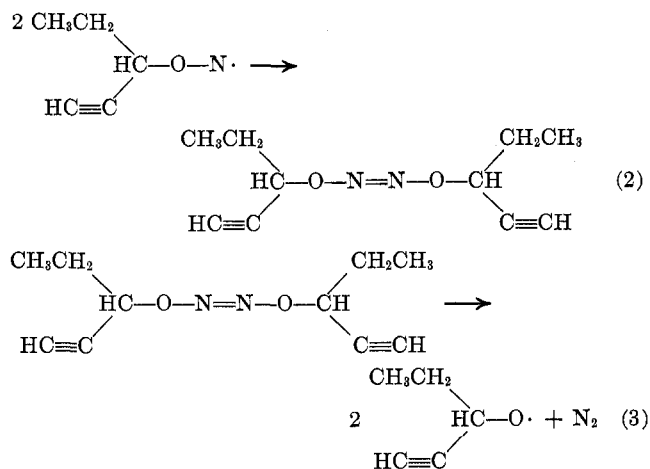
(2) J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **79**, 2480 (1957).

ticularly effective at initiating radical reactions, and in most instances must depend on initiation by other radical species. In many reactions of nitric oxide with neutral molecules, nitrogen dioxide is considered to be the initiating species and arises through air oxidation of nitric oxide. Under our experimental conditions no special attempt was made to scrupulously exclude oxygen from the system; however, it is thought that air was removed from the reaction zone and, hence, did not serve as a reagent for the formation of nitrogen dioxide, because of the absence of reddish-brown coloration in the gas phase and of products containing carbon-nitrogen bonding.<sup>3</sup>

It is proposed that initiation in the 1-pentyne-nitric oxide reaction is spontaneous making alkyl free radicals available for interaction with nitric oxide. Such spontaneous initiation by reactions between molecules has been suggested in a number of reactions.<sup>4</sup> The action of nitric oxide with the radical intermediate is suggested to occur through the formation of a nitroxymethane derivative (eq 1) which rapidly associates yielding an



organic ester of hyponitrous acid (eq 2). This ester being unstable decomposes with the formation of alkoxy radicals and nitrogen (eq 3). These reactions are in ac-



cord with the known chemistry of inorganic nitroso compounds<sup>5</sup> and hyponitrous esters,<sup>6</sup> and this type of mechanism has been employed to explain the formation of products from the reaction of nitric oxide with pentaphenylethane.<sup>7</sup> This latter study represents the only known instance where alkyl radicals react with nitric oxide to give dialkylmethane nitroso compounds.

Further known reactions of alkoxy radicals can explain the formation of the observed products, 1-pentyn-3-ol and 1-pentyn-3-one. Nitration of the alcohol by nitric oxide yields the nitrate ester. This series of re-

actions constitutes a plausible mechanism which is consistent with the available experimental results and with the established properties of analogous compounds.

#### Experimental Section

To a 100-ml round-bottom flask fitted with magnetic stirrer was introduced 15.0 g (0.22 mol) of 1-pentyne and the flask connected to a vacuum manifold containing a 2-l. expansion bulb through a Dry Ice-Acetone condenser. The total system was deaired by passing through three freeze-thaw cycles while under vacuum. Nitric oxide (3.78 g, 0.26 mol) was charged into the system and the mixture allowed to come to ambient temperature. The initial pressure was 565 mm; after stirring for 28 hr the pressure was 525 mm. A mass spectral analysis of the gaseous materials showed the presence of nitric oxide and nitrogen. A total of 2.24 g (0.075 mol) of nitric oxide was recovered (40.7% consumed). The contents of the reaction flask were examined by glc and found to consist of 1-pentyne and three major products identified as 1-pentyn-3-ol, 1-pentyn-3-one, and 1-pentyn-3-nitrate.

In a similar reaction with 1-hexyne (8.2 g, 0.1 mol), 1.5 gm (0.05 mol) of nitric oxide was consumed (41%) and the corresponding alcohol, ketone and nitrate ester found.

When 15.0 g (0.18 mol) of 1-pentyn-3-ol was treated with 3.78 g (0.126 mol) of nitric oxide, a total of 2.0 g (0.066 mol) nitric oxide was consumed (52.9%) and the reaction products were 1-pentyn-3-one and 1-pentyn-3-nitrate.

**Registry No.**—Nitric oxide, 10102-43-9; 1-pentyne, 627-19-0.

**Acknowledgment.**—This work was conducted under the sponsorship of the Advanced Research Projects Agency under Army Ordnance Contract DA-01-021 ORD 11909. The technical assistance of Mr. James O. Woods and Mrs. Carolyn Haney is appreciated.

#### Novel *cis*-Hydroxylation with Nitrous acid

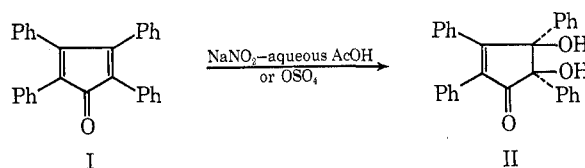
S. RANGANATHAN\* AND S. K. KAR

Department of Chemistry,  
Indian Institute of Technology, Kanpur, U. P., India

Received April 1, 1970

We report a unique high yield *cis*-hydroxylation with sodium nitrite-aqueous acetic acid. A benzene solution of tetraphenylcyclopentadienone (I, tetracyclone) when reacted with sodium nitrite in aqueous acetic acid at 0°, conditions generally employed for diazotization, gave after work-up a white crystalline compound, mp 191°, in 85% yield which was subsequently identified as *cis*-2,3-dihydroxy-2,3,4,5-tetraphenylcyclopent-4-en-1-one (II) on the basis of ir, nmr, analysis, and by direct comparison with an authentic sample.<sup>1</sup>

The stereochemical assignment was confirmed to be *cis* through preparation of II by treatment of tetra-



\* Author to whom correspondence should be addressed.

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(6) N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, pp 1-2.

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