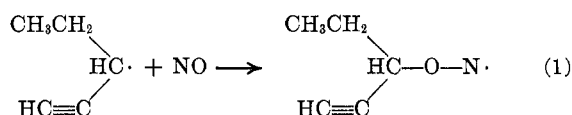
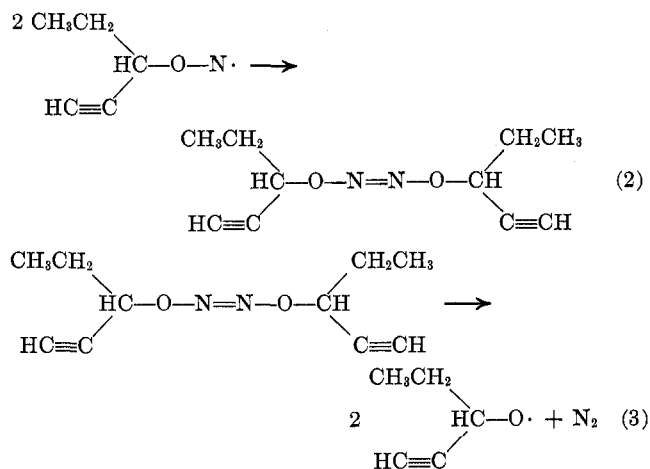


ticularly effective at initiating radical reactions, and in most instances must depend on initiation by other radical species. In many reactions of nitric oxide with neutral molecules, nitrogen dioxide is considered to be the initiating species and arises through air oxidation of nitric oxide. Under 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.³

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.⁴ 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 compounds⁵ and hyponitrous esters,⁶ and this type of mechanism has been employed to explain the formation of products from the reaction of nitric oxide with pentaphenylethane.⁷ 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

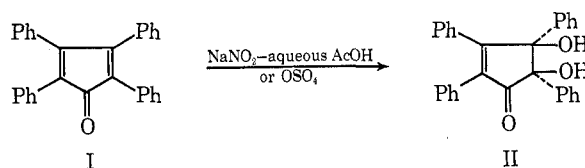
S. RANGANATHAN* AND S. K. KAR

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.¹

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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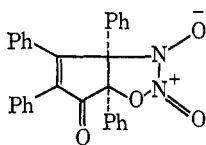
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cyclone with osmium tetroxide. The reaction of $\text{NaNO}_2\text{-H}^+$ with olefins has been extensively studied;²⁻⁵ however, no *cis*-hydroxylation has been reported with this reagent.

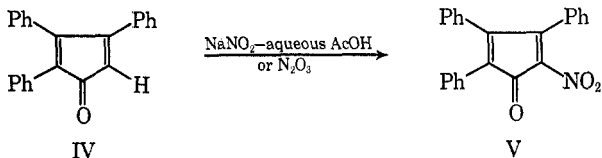
Since, at low temperatures dinitrogen trioxide has been recognized as the reactive species involved in sodium nitrite-aqueous acetic acid reactions, it was considered probable that this reagent could bring about transformation leading to II. Following this reasoning, an ice-cooled dry benzene solution of I was treated in drops, with a dry benzene solution of dinitrogen trioxide until the intense pink color of I was completely discharged. The reaction is extremely rapid and takes only few minutes for completion. Removal of benzene under anhydrous conditions gave a colorless foamy material which has been tentatively assigned the structure III.⁹ The compound III was tremendously sensi-



III

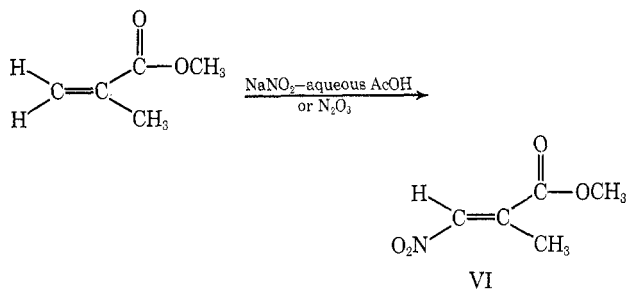
tive to moisture and on keeping, even under best possible "dry" conditions, was converted to the dihydroxy compound II. Compound III could be transformed exclusively to II by treatment with water, aqueous acetic acid, and aqueous dioxane.¹⁰

With a view to further understand the hydroxylation reaction the action of sodium nitrite-aqueous acetic acid and also dinitrogen trioxide on the closely related 3,4,5-triphenylcyclopentadien-1-one (IV, tetracyclone) was carried out. Surprisingly, both these reagents gave as the sole isolable product the orange-brown 2-nitro-3,4,5-triphenylcyclopentadien-1-one (V). Structure V is based on ir, nmr, and analysis.



Similarly methyl methacrylate under conditions employed in the $\text{I} \rightarrow \text{II}$ change gave the nitro olefin

(VI) (structural assignment supported by ir, nmr, and analysis⁵).



VI

Compounds V and VI are products expected on basis of known pathways involved in dinitrogen trioxide initiated reactions.^{4,5} In these cases the possibility present for the elimination of HNO , which is not possible in the case of I, gives direction to the overall reaction.¹¹

The formation of II from either I or III could be rationalized on basis of several pathways and this facet of the transformation is currently being examined in detail.

Experimental Section¹²

Preparation of *cis*-2,3-Dihydroxy-2,3,4,5-tetraphenylcyclopent-4-en-1-one (II). A. From I and Sodium Nitrite in Acetic Acid-Water-Benzene.—A stirred benzene solution of tetracyclone (0.5 g, 1.3 mmol, 10 ml) was treated with acetic acid-water (3:2, 5 ml), and the mixture was cooled to 0°. Solid sodium nitrite (0.5 g, 7 mmol) was gradually introduced over a period of 15 min while maintaining the temperature below 5°. The colorless reaction mixture was stirred for an additional 30 min. The layers were separated; the organic layer was washed several times with water, dried (MgSO_4), and evaporated. The residue on crystallization from benzene gave 0.46 g (85%) of II: mp 190–191° dec; this melting point was not depressed by admixture with an authentic sample,¹ mp 190–191°; ir [$\lambda_{\text{max}}^{\text{KBr}}$ 2.9 (OH), 5.9 ($>\text{C}=\text{O}$) μ]; nmr [δ_{CDCl_3} 7.2 (aromatic protons)].

Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{O}_3$: C, 83.25; H, 5.26. Found: C, 83.52; H, 4.98.

B.—From I and Dinitrogen Trioxide in Acetic Acid-Water-Benzene.—A stirred benzene solution of tetracyclone (0.2 g, 0.52 mmol, 5 ml) was treated with acetic acid-water (3:2, 5 ml) and the mixture was cooled to 0°. A dilute dry benzene solution of dinitrogen trioxide¹³ was added dropwise until decolorization was complete (~10 ml). The clear solution was stirred for additional 30 min, the layers separated, and the organic layer was washed several times with water, dried (MgSO_4), and evaporated. The residue on crystallization from benzene gave 0.182 g (85%) of II, mp 192–193° dec.

C.—From I and Sodium Nitrite in Sulfuric Acid-Water-Benzene.—A stirred benzene solution of tetracyclone (0.5 g, 1.3 mmol, 10 ml) was treated with sulfuric acid-water (3:2, 5 ml) and the mixture was cooled to 0°. Solid sodium nitrite (0.5 g, 7 mmol) was gradually introduced over a period of 25 min while maintaining the temperature below 5°. The colorless reaction mixture was stirred for an additional 30 min. The layers were separated and the organic layer was washed several times with water, dried (MgSO_4), and evaporated. The residue on crystallization from benzene gave 0.378 g (70%) of II, mp 190–191° dec.

D.—From I and Osmium Tetroxide.—An ice-cooled dry ether solution of tetracyclone (0.5 g, 1.3 mmol, 20 ml) was treated

(11) The more promising examples, 2,3-dihydroxytetracyclone and *trans*-dibenzoylethylene, were not affected under conditions of $\text{I} \rightarrow \text{II}$ change; however, 2,3-diphenylglyoxal, gave the *cis*-diol in 50% yield [H. Biltz, *Justus Liebigs Ann. Chem.*, **363**, 156 (1909), and ref 1].

(12) All melting points and boiling points are uncorrected. Ir spectra were taken on Perkin-Elmer Model 521 spectrometer. Nmr spectra were obtained on a Varian A-60 spectrometer using TMS as an internal reference. Microanalyses were done in the microanalytical laboratory of the Department of Chemistry, I. I. T., Kanpur.

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(9) Initially we preferred an open nitro nitroso dimer structure for III. Subsequently a referee suggested the cyclic structure and provided persuasive arguments in favor of this structure [J. R. Park and D. L. H. Williams, *Chem. Commun.*, 332 (1969), and unpublished work]. We are grateful to this referee for the valuable suggestion.

(10) Reaction of the adduct III with excess dry methanol lead to *instant* appearance of the characteristic pink color of tetracyclone and tlc of the reaction mixture taken immediately indicated reversal to I. This unexpected observation has no precedence and is being currently examined.

with osmium tetroxide (0.33 g, 1.3 mmol) and pyridine (1 ml) and the mixture was stirred at room temperature for 72 hr. The insoluble complex was decomposed with mannitol (5 g) in 10% aqueous potassium hydroxide (20 ml) and stirring continued for 12 hr. The reaction mixture was extracted with methylene chloride, the organic layer washed with water and dried (MgSO_4), and solvents were evaporated. The residue on crystallization from benzene gave 0.34 g (63%) of II, mp 190–191° dec. This melting point was not depressed by admixture with an authentic sample,¹ mp 190–191° dec.

Reaction of I with Dinitrogen Trioxide in Benzene. Preparation of III.—A stirred and ice-cooled dry benzene solution of tetracyclone (0.5 g, 1.3 mmol, 10 ml) was treated dropwise with a dry benzene solution of dinitrogen trioxide until decolorization was complete (~10 ml). The solvent was removed *in vacuo* and without heating under rigorously dry conditions to give III as a noncrystalline solid: mp 95° dec; ir [$\lambda_{\text{max}}^{\text{KBr}}$ 5.7 ($>\text{C}=\text{O}$), 6.5, 7.5 μ ; also present 2.85 (OH) 5.9 ($>\text{C}=\text{O}$) μ due to decomposition to II].

Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4$: N, 6.08. Found: N, 6.01.

Reactions of III. A. With Aqueous THF.—Aqueous THF (3:2, 5 ml) was added to 0.1 g of III. The solution became pink owing to the formation of some I. The color disappeared on standing. The colorless reaction mixture was extracted with benzene and dried (MgSO_4), and solvent evaporated to yield II, mp 191–192° dec.

B. With Aqueous Acetic Acid.—Aqueous acetic acid (3:2, 5 ml) was added to 0.1 g of III. The pinkish color due to the formation of some I, disappeared immediately. The colorless reaction mixture was extracted with benzene, the organic layer was washed with water and dried (MgSO_4), and solvents were evaporated to yield II, mp 190–191° dec.

C. With Anhydrous Methanol.—Absolute methanol (5 ml) was added to 0.1 g of III. The solution instantly became pink owing to the formation of I. The color did not fade on long standing. Evaporation of solvents gave pure I, mp 223°.

Preparation of 3,4,5-Triphenylcyclopentadien-1-one IV (Tricyclone).—The blue tricyclone was prepared by the condensation of benzil with phenylacetone,¹⁴ mp 292–293° dec (lit.¹⁴ mp 292–294°).

Reactions of Tricyclone. A. With Sodium Nitrite Acetic Acid-Water-Benzene.—A stirred benzene solution of tricyclone (0.5 g, 1.62 mmol, 10 ml) was treated with acetic acid:water (3:2, 5 ml) and cooled to 0°. Solid sodium nitrite (0.5 g 7 mmol) was gradually introduced over a period of 15 min while maintaining the temperature below 5°. The brown reaction mixture was stirred for additional 30 min. The layers were separated, the organic layer was washed several times with water and dried (MgSO_4), and solvents were evaporated. The residue on crystallization from benzene-hexane mixture gave 0.45 g (79%) of V: mp 158–160° dec; ir [$\lambda_{\text{max}}^{\text{KBr}}$ 5.8 ($>\text{C}=\text{O}$), 6.5 ($-\text{NO}_2$, asymmetric), 7.3 ($-\text{NO}_2$, symmetric) μ]; nmr [δ_{CDCl_3} 7.2 (aromatic protons)].

Anal. Calcd for $\text{C}_{23}\text{H}_{15}\text{NO}_3$: C, 78.18; H, 4.24; N, 3.96. Found: C, 78.08; H, 4.6; N, 3.63.

B. With Dinitrogen Trioxide under Anhydrous Conditions and Treatment with Absolute Methanol.—A stirred and ice-cooled dry benzene solution of tricyclone (0.5 g, 1.62 mmol, 10 ml) was treated dropwise with a dry benzene solution of dinitrogen trioxide (10 ml). Tricyclone color disappeared rapidly and the solution became chocolate brown. Solvents were removed *in vacuo* without heating and under rigorously dry conditions. Absolute methanol (10 ml) was added. No tricyclone color reappeared even on standing. Solvents were removed and the residue on crystallization from benzene-hexane mixture gave 0.46 g (80%) of V, mp 159–160° dec.

Reaction of Methyl Methacrylate with Sodium Nitrite Acetic Acid-Water-Benzene.—A stirred benzene solution of methyl methacrylate (5 g, 50 mmol, 10 ml) was treated with acetic acid:water (3:2, 20 ml) and the mixture was cooled to 0°. Solid sodium nitrite (5 g, 70 mmol) was gradually introduced over a period of 15 min while maintaining the temperature below 5°. The reaction mixture was stirred for additional 6 hr. The layers were separated, the organic layer was washed several times with water and dried (MgSO_4), and solvents were evaporated. The residue on distillation gave 3.6 g (45%) of VI: bp 90° (4 mm);⁵ ir [$\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.78 ($>\text{C}=\text{O}$), 6.1 ($\text{C}=\text{C}$), 6.5 ($-\text{NO}_2$, asymmetric),

7.4 ($-\text{NO}_2$, symmetric) μ]; nmr [δ_{CCl_4} 2.2 (d, $-\text{CH}_3$), 3.8 (s, $-\text{OCH}_3$), 7.6 (q, H)].

Anal. Calcd for $\text{C}_8\text{H}_7\text{NO}_4$: C, 41.37; H, 4.82; N, 9.64. Found: C, 41.4; H, 4.9; N, 9.4.

Registry No.—Nitrous acid, 7782-77-6; II, 25716-03-4; III, 25662-49-1; V, 25665-22-9; VI, 25662-50-4.

Acknowledgments.—We thank Dr. Nitya Nand, CDRI, Lucknow, for providing nmr facilities. Financial assistance by way of a Lady Tata Memorial Trust Scholarship (SKK) is gratefully acknowledged.

Preparation of Optically Pure Diastereomeric 2-Methyl-2,3-dihydrobenzothiophene 1-Oxides and Comments on the Mechanism of Reduction of Cyclic Sulfones¹

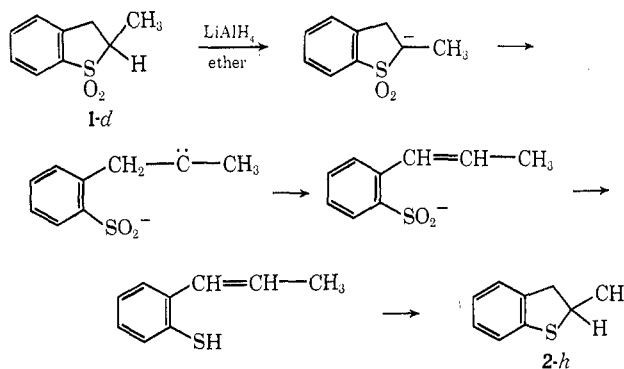
THOMAS A. WHITNEY² AND DONALD J. CRAM³*

Contribution No. 2564 from the Department of Chemistry,
University of California, Los Angeles, California 90024

Received April 3, 1970

As a part of the study of electrophilic substitution at saturated carbon,³ the title compounds were prepared as follows. Optically pure 2-methyl-2,3-dihydrobenzothiophene-2-*d* (or -2-*h*) 1-dioxide [e.g., (+)-1-*h*] was reduced with lithium aluminum hydride to (-)-2-*h*, which was oxidized under controlled conditions to give a mixture of optically pure diastereomers (+)-3-*h* and (-)-3-*h*, separable by column chromatography. Although the 2,3-dihydrobenzothiophene 1-oxide system was found to be unstable toward *tert*-butyl alcohol-potassium *tert*-butoxide (thus precluding study of the stereochemistry of electrophilic substitutions), the reactions involved in the preparation of the compounds provide insight into the mechanism of the reduction of cyclic five-membered ring sulfones to sulfides.

Bordwell and McKellin⁴ investigated the behavior of a variety of sulfones with lithium aluminum hydride and found that generally only cyclic four- and five-



* Author to whom correspondence should be addressed.

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(2) National Science Foundation Predoctoral Fellow, 1962–1966.

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