

weak signals for the di-*t*-butyl nitroxide radical (VIII). As soon as ozone was passed into the solutions, by the technique already described, the signals greatly increased. Shortly thereafter signals for the 2-methyl-2-nitrobutane anion radical<sup>17</sup> also appeared (see description under *t*-butylamine ozonation above) very weakly in the methylene chloride reaction mixture but of moderate intensity in the other two solutions. No signal for the ozonate anion radical was observed in any of these reaction mixtures. However, when a 1:4 mixture of *t*-butylamine and di-*t*-butylamine in pentane was ozonized at  $-120^\circ$  by the above technique, a strong signal for the ozonate anion radical<sup>5</sup> (see description under ozonation of *t*-butylamine, above) immediately appeared along with a weaker signal for the di-*t*-butyl nitroxide radical. *t*-Butylamine appears to be more reactive toward ozone than di-*t*-butylamine. Ozonation of di-*t*-butyl nitroxide in pentane at  $-120^\circ$  resulted in a decrease in the nitroxide triplet, but no formation of the 2-methyl-2-nitropropane anion radical signal. Epr spectra of solutions of di-*t*-butylhydroxylamine in methylene chloride, pentane, and Freon 11 at  $-90^\circ$  all showed signals for the di-*t*-butyl nitroxide radical (VIII). When ozone-nitrogen was introduced into the solution, the signal weakened in intensity or disappeared (in case of  $\text{CH}_2\text{Cl}_2$ ).

(B) **Product Determination.**—In a typical experiment, a solution of 2.36 mmol of di-*t*-butylamine (VII) in 15 ml of chloroform was ozonized at  $-60^\circ$  with an ozone-nitrogen stream containing 6.5 mmol of ozone. The amount of ozone reacting was determined by titrating the iodide trap and subtracting the amount found there from the total amount of ozone employed. A cold trap following the reaction vessel in the reaction train contained no products after the ozonation. The reaction mixture gave a positive iodide test for peroxide but a negative lead tetraacetate test for hydroperoxide.<sup>18</sup> Determinations of the liquid

(18) R. Criegee, H. Pilz, and H. Flygare, *Ber.*, **72**, 1799 (1939).

products were by glpc (see above). Di-*t*-butylammonium chloride was determined by evaporation of an aliquot of the reaction mixture to dryness and weighing the vacuum-dried residue. It was identified by comparison of its ir spectrum (Nujol mull) with that of an authentic sample; the ir spectrum also showed the absence of di-*t*-butyl hydroxylammonium chloride. The results are shown in Table I (expt 1). In another experiment the ozonation was not carried to completion. The di-*t*-butylammonium chloride was extracted from the reaction mixture with water and determined by titration for chloride with standard silver nitrate solution. Ethereal hydrogen chloride was then added to the organic layer; evaporation and determination of the residue by weighing gave the yield of unreacted di-*t*-butylamine.

**Reactions of *t*-Butylamine and Di-*t*-butylamine with Phosgene in Chloroform at  $-65^\circ$ .**—Phosgene was passed into a solution of 0.5 ml of *t*-butylamine in 8 ml of chloroform at  $-65^\circ$  for several minutes. An ir spectrum of the reaction mixture showed a strong isocyanate peak ( $2270\text{ cm}^{-1}$ ) but no urea peak. Addition of *t*-butylamine to the reaction mixture at room temperature eliminated the isocyanate peak and gave rise to a strong urea carbonyl peak ( $1630\text{ cm}^{-1}$ ). Passage of phosgene into a chloroform solution of di-*t*-butylamine under the same conditions gave no appreciable reaction, as indicated by ir spectra.

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## Ozonation of Amines. V.<sup>1</sup> Di-*t*-butyl Nitroxide

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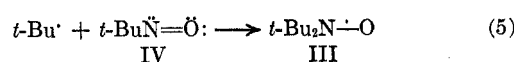
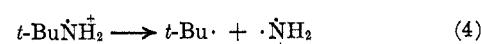
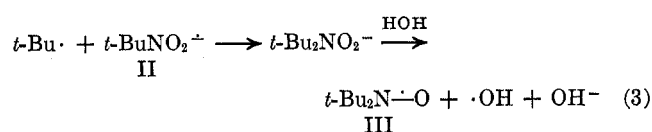
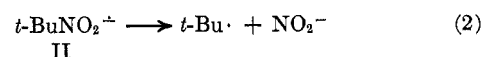
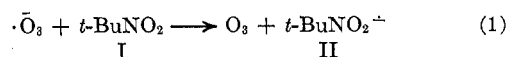
Received January 2, 1970

Ozonation of di-*t*-butyl nitroxide occurs with ease giving 2-methyl-2-nitropropane and tri-*t*-butyl nitroxide as the major initial products. Ozonation of tri-*t*-butyl nitroxide gives 2-methyl-2-nitropropane, *t*-butyl alcohol, and acetone as major products. Minor products of the ozonations are 2-methyl-2-nitrosopropane, isobutene, di-*t*-butyl peroxide, and (in chloroform solution) *t*-butyl chloride and di-*t*-butylhydroxylammonium chloride. Reaction mechanisms are proposed, involving initial electrophilic ozone attacks on the nitroxides.

In earlier papers we have reported the detection of the stable radical di-*t*-butyl nitroxide<sup>2</sup> among the products of ozonation of *t*-butylamine<sup>1,3</sup> and di-*t*-butylamine.<sup>1</sup> The present paper deals largely with a study of the ozonation of this interesting stable radical, but also discusses briefly the source of the material in the above mentioned ozonations.

Di-*t*-butyl nitroxide appears to be only a minor by-product in the ozonation of *t*-butylamine;<sup>1,3</sup> although it was detected by epr in ozonations carried out at  $-78^\circ$  or higher, the only radical signal observed during ozonations carried out at  $-90^\circ$  or below was that for the ozonate anion radical.<sup>1</sup> Other products obtained in trace amounts from ozonation of *t*-butylamine in chloroform were *t*-butyl alcohol, acetone, and isobutane.<sup>3</sup> Two sources of di-*t*-butyl nitroxide during the reaction between sodium metal and 2-methyl-2-nitropropane (I) have been suggested.<sup>2</sup> One involves hydrolysis of a salt, thought to be sodium di-*t*-butyl-

hydroxylamine oxide and formed by attack of *t*-butyl radicals upon the initially formed 2-methyl-2-nitropropane anion radical (eq 3); the *t*-butyl radicals arose from decomposition of the nitroalkane anion radical (eq 2). The other source involved attack of *t*-butyl radicals on 2-methyl-2-nitrosopropane (eq 5). Either or both of these routes could also be the source of di-*t*-butyl nitroxide during ozonation of *t*-butylamine. A major product is 2-methyl-2-nitropropane<sup>3</sup> (I), and it



(1) For paper IV of this series, see P. S. Bailey, J. E. Keller, and T. P. Carter, Jr., *J. Org. Chem.*, **35**, 2777 (1970).

(2) A. K. Hoffmann, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, **86**, 639 (1964).

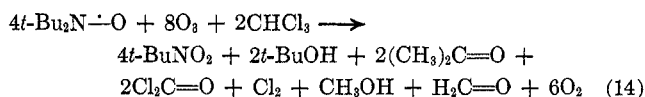
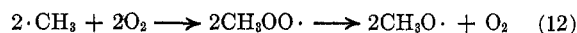
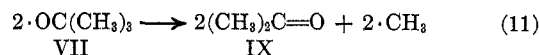
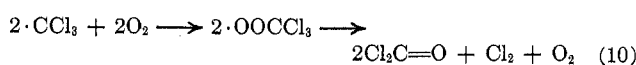
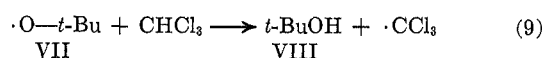
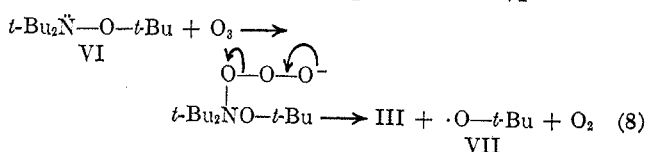
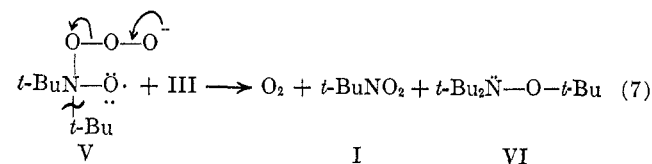
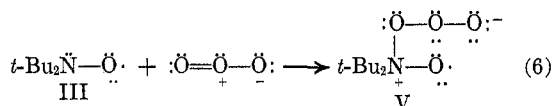
(3) P. S. Bailey and J. E. Keller, *J. Org. Chem.*, **33**, 2680 (1968).

could conceivably be converted to the corresponding anion radical (II) by the ozonate anion radical (eq 1). Water is a minor product of the ozonation of *t*-butylamine.<sup>3</sup> However, a major intermediate in the ozonation of *t*-butylamine is 2-methyl-2-nitrosopropane<sup>3</sup> (IV). The source of *t*-butyl radicals necessary to convert it to di-*t*-butyl nitroxide (eq 5) could either be as described above, or else decomposition of the *t*-butylamine cation radical (eq 4). The occurrence of trace amounts of acetone, *t*-butyl alcohol, and isobutane among the products of ozonation of *t*-butylamine<sup>3</sup> is also indicative of the production of *t*-butyl radicals during the ozonation, although the first two of these could also arise from ozonation of di-*t*-butyl nitroxide, as will be seen.

Di-*t*-butyl nitroxide (III) was shown to be an initial product in the ozonation of di-*t*-butylamine.<sup>1</sup> Similar nitroxides have also been reported to be not only initial, but also major products of ozonation of certain aromatic and alicyclic secondary amines.<sup>4</sup> Because of this it was most important to study the ozonation of di-*t*-butyl nitroxide and to compare the results with those of the ozonation of di-*t*-butylamine.<sup>1</sup>

The ozonation of di-*t*-butyl nitroxide was carried out in chloroform at  $-65^\circ$ , carbon tetrachloride at  $-20^\circ$ , and toluene at  $-78^\circ$  with an ozone-nitrogen stream containing 1.0 to 2.2 mol equiv of ozone. The results are shown in Table I. The major product in all cases was 2-methyl-2-nitrosopropane (I). Only in those cases where the ozonation was not carried out to completion (all of the di-*t*-butyl nitroxide used) was any 2-methyl-2-nitrosopropane (IV) a product. The *t*-butyl group lost in the formation of the nitroalkane (I) was found in the products largely in the forms of *t*-butyl alcohol (VIII), acetone (IX), and tri-*t*-butyl nitroxide (VI). The latter was detected, however, only in those cases where ozonation was not carried to completion. Minor products were di-*t*-butyl peroxide, isobutene, *t*-butyl chloride, and di-*t*-butylhydroxylammonium chloride; the last two, of course, were obtained only from ozonations in chloroform and/or carbon tetrachloride.

We suggest eq 6-13 as a description of the route to the major products from ozonation of III in chloroform solution. Summed together these give eq 14.



Since di-*t*-butyl nitroxide (III) is very reactive toward ozone, which is diamagnetic, we suggest that in the initial reaction III behaves as a nucleophile (eq 6) rather than a radical, just as do amines. Interaction of the nitroxide-ozone adduct (V) with another molecule of the nitroxide should give 3-methyl-3-nitrosopropane (I), the major product of the ozonation, and tri-*t*-butyl nitroxide (VI). Di-*t*-butyl nitroxide is known to be a vigorous free-radical scavenger; its reaction with *t*-butyl radicals to give tri-*t*-butyl nitroxide occurs with great ease.<sup>2</sup> Evidence that VI is an initial product of the ozonation is that the yield decreased significantly as the amount of ozone employed increased (*cf.* experiments 1, 2, and 4-6). The tri-*t*-butyl nitroxide (VI) is quite reactive toward ozone, although not so reactive as is di-*t*-butyl nitroxide (III). Ozonation of the tri-*t*-butyl nitroxide (VI) in a separate experiment gave the same products as obtained from ozonation of di-*t*-butyl nitroxide, as predicted by eq 8-11. Due to the greater reactivity of the di-*t*-butyl nitroxide (III), however, only weak epr signals for III were detected in the mixture. Reaction 10 has previously been suggested by Cadogan, *et al.*<sup>5</sup>

The major reaction course for ozonation of di-*t*-butyl nitroxide gives no explanation for the minor products 2-nitroso-2-methylpropane (IV), di-*t*-butylhydroxylammonium chloride, isobutene, *t*-butyl chloride, and di-*t*-butyl peroxide. The latter one probably arises from a minor fate of the *t*-butoxy radicals (VII) obtained in reaction 8. The others appear to arise, at least largely, from attack of either chlorine (from eq 10) or hydrogen chloride (possibly from some ozone attack on chloroform) on the starting di-*t*-butyl nitroxide. These are the products reported from such interactions,<sup>6</sup> as has been confirmed in our laboratory. This is, certainly, the most reasonable route to di-*t*-butylhydroxylammonium chloride. It is likely, however that there are alternative routes to the other minor products, since they are also obtained from ozonation of III in carbon tetrachloride; carbon tetrachloride is not appreciably attacked by ozone and reaction 9, of course, is specific for chloroform. This is especially true of isobutene, which is also obtained from the ozonation of III in toluene. It is possible that the *t*-butyl radical released in reaction 7 has some degree of freedom. It so, it could extract chlorine from the medium, to give *t*-butyl chloride, or lose a hydrogen (perhaps to *t*-butoxy radicals) to produce isobutene. A possible alternative route to 2-methyl-2-nitrosopropane (IV) is shown by eq 15, in competition with reaction 7. The *t*-butyl alcohol obtained in carbon tetrachloride solution could arise by abstraction of hydrogen by *t*-butoxy

(5) J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965).

(6) (a) A. K. Hoffmann and A. T. Henderson, *J. Amer. Chem. Soc.*, **83**, 4671 (1961); (b) A. M. Feldman, private communication.

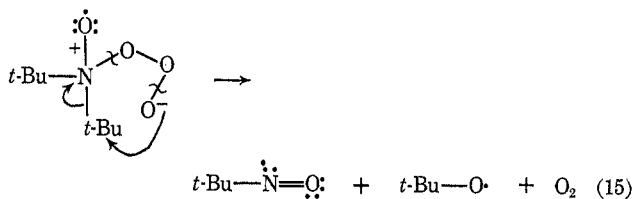
(4) S. D. Razumovskii, A. L. Buchachenko, A. B. Shapiro, E. G. Rozantsev, and G. E. Zaikov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **103**, 1086 (1968).

TABLE I  
 OZONATIONS OF DI-*t*-BUTYL NITROXIDE AND DI-*t*-BUTYLHYDROXYLAMINE

Expt	Solvent <sup>c</sup> (ml)	Compd. <sup>b</sup> (mmol)		O <sub>3</sub> evolved, mmol (%) <sup>d</sup>	O <sub>3</sub> / reacted compd <sup>d</sup>	O <sub>2</sub> evolved, mmol (%) <sup>d</sup>	O <sub>2</sub> evolved, mmol (%) <sup>d</sup>	t-BuNO <sub>2</sub> , mmol (%) <sup>e</sup>	t-BuN=O, mmol (%) <sup>e</sup>	t-BuNHOH, mmol (%) <sup>e</sup>	t-BuOH, mmol (%) <sup>e</sup>	Acetone, mmol (%) <sup>e</sup>	Isobutene, mmol (%) <sup>e</sup>	(t-BuO) <sub>2</sub> , mmol (%) <sup>e</sup>	t-BuCl, mmol (%) <sup>e</sup>	Others, mmol (%) <sup>e</sup>	N <sup>4</sup> , mmol (%) <sup>e</sup>	t-Bu <sup>5</sup> , mmol (%) <sup>e</sup>
		Start- ing	React- ing															
1	CHCl <sub>3</sub> (15)	3.00	3.00	3.2 (58)	1.8	3.1 (60)	2.64 (88)	0 (0)	0.27 (9)	0.93 (31)	0.88 (29)	0.04 (1)	0.07 (2)	0.08 (3)	0 (0)	2.91 (97)	2.34 (78)	
2	CHCl <sub>3</sub> (15)	3.00	3.00	3.1 (60)	1.7	3.1 (60)	2.74 (91)	0 (0)	0.17 (6)	...	...	...	...	...	0.06* [2]	2.91 (97)	...	
3	CHCl <sub>3</sub> (25)	5.00	5.00	...	1.5	...	4.22 (84)	0 (0)	0.60 (12)	1.30 (26)	1.16 (23)	0.45 (9)	...	0.18 (4)	...	4.82 (96)	3.69 (74)	
4	CHCl <sub>3</sub> (15)	5.00	4.33	3.1 (62)	1.2	3.1 (62)	3.02 (70)	0.46 (11)	0.31 (7)	0.88 (20)	0.63 (15)	0.53 (12)	0.14 (3)	0.30 (7)	0.38* (9)	4.17 (96)	3.69 (85)	
5	CHCl <sub>3</sub> (15)	9.02	4.64	...	1.1	...	...	...	...	...	...	...	...	...	1.28* (28)	...	...	
6	CHCl <sub>3</sub> (6)	2.10	0.43	3.4 (68)	1.2	...	...	...	...	...	...	...	...	...	0.13* (30)	...	...	
7	CCl <sub>4</sub> (15)	5.00	4.83	3.7 (74)	1.0	3.4 (68)	3.39 (70)	0.37 (8)	...	0.67 (14)	0.46 (10)	0.29 (6)	0.28 (6)	0.06 (1)	0.82* (17)	4.58 (95)	3.68 (76)	
8	Toluene (15)	5.00	4.21	2.9 (81)	1.2	2.9 (81)	2.92 (69)	...	0	0.91 (22)	0.29 (7)	0.27 (6)	0.08 (2)	0	1.06* (25)	3.98 (95)	3.75 (89)	
9	CHCl <sub>3</sub> (15)	3.00	2.98	2.9 (81)	1.2	2.9 (81)	1.46 (49)	0.14 (5)	0.44 (15)	0.69 (23)	0.47 (16)	0.18 (6)	...	0.49 (16)	0.39* (13)	2.43 (81)	2.66 (89)	

<sup>a</sup> The ozonations in CHCl<sub>3</sub> were carried out at -65°, the one in CCl<sub>4</sub> at -20°, and the one in toluene at -78°. In runs 1-8 the compound ozonized was di-*t*-butyl nitroxide, whereas in run 9 di-*t*-butylhydroxylamine was ozonized. <sup>b</sup> The mmols of nitrogen compound reacting is equal to mmols starting compound minus mmols of same compound detected at end of experiment. <sup>c</sup> All ozonations were with ozone-nitrogen. <sup>d</sup> Ratio of ozone reacting to nitrogen compound reacting. <sup>e</sup> Per cent yield of molecular oxygen is based on mmols of ozone reacting. <sup>f</sup> Percentage yields of organic products are based on mmols of starting nitrogen compound which reacted. <sup>g</sup> Per cent accounting of nitrogen in products from starting amine. <sup>h</sup> Per cent accounting in products of second *t*-butyl group (which is lost in production of the nitro compound). <sup>i</sup> Not determined. <sup>j</sup> Tri-*t*-butyl nitroxide. <sup>k</sup> Di-*t*-butyl nitroxide.

radicals from various sources, including *t*-butyl and methoxy radicals.



Experiment 9 of Table I shows the results of ozonation of di-*t*-butylhydroxylamine rather than of di-*t*-butyl nitroxide (III). The products are the same as those obtained from ozonation of di-*t*-butyl nitroxide, although the proportions are different. As discussed in the preceding paper, these results are hard to interpret, but are, at least partially, due to oxidation of the hydroxylamine to the nitroxide by molecular oxygen.

### Experimental Section

**Materials.**—Tri-*t*-butyl nitroxide (VI) was prepared by the procedure of Hoffmann, *et al.*,<sup>2</sup> bp 85° (11 mm). The sources of the other materials were described in the accompanying paper.<sup>1</sup>

**General Equipment and Procedures.**—The ozonation, epr, glpc, and ir equipment and procedures were adequately described in the accompanying paper.<sup>1</sup> In the glpc procedure, tri-*t*-butyl nitroxide (VI) was determined under the same conditions as was di-*t*-butyl nitroxide (III).<sup>1</sup>

**Ozonation of Di-*t*-butyl Nitroxide (III).**—The ozonations were carried out exactly as described for di-*t*-butylamine in the accompanying paper.<sup>1</sup> Glpc determinations were carried out as described above and in the accompanying paper.<sup>1</sup> The di-*t*-butylhydroxylammonium chloride was determined by evaporation of the reaction mixture to dryness and weighing the vacuum dried residue; it was identified by comparison of its infrared spectrum with that of an authentic sample. The results are shown in Table I.

**Ozonation of tri-*t*-butyl nitroxide (VI)** was carried out as described for III, above, except that the ozone absorption was slower (some ozone passed into the trap, throughout); the glpc determinations were performed qualitatively. The products were the same as those obtained from ozonation of di-*t*-butyl nitroxide.

In another experiment a microozonation of VI in pentane at -120° was monitored by epr.<sup>7</sup> The di-*t*-butyl nitroxide triplet was present at the beginning of the ozonation but decreased in size and remained weak as ozone was introduced; this indicates that di-*t*-butyl nitroxide is a product of the ozonation, but is more reactive than tri-*t*-butyl nitroxide.

**Ozonation of Di-*t*-butylhydroxylamine.**—The ozonation was complicated by the ease with which the hydroxylamine was oxidized to di-*t*-butyl nitroxide. It was necessary to purify the hydroxylamine immediately prior to use by washing with cold pentane on a Büchner funnel. The solid was quickly dried under vacuum and was weighed and added to the solvent which had previously been purged with nitrogen for several hours. Oxygen was completely purged from the silica gel column containing the ozone before the reaction vessel was placed in the gas stream. Even then, the pale red color of the nitroxide was present in the reaction mixture and increased during the ozonation. During determination of products the color deepened due to conversion of unreacted amine to nitroxide. The results are shown in Table I, experiment 9. In another experiment a microozonation in methylene chloride at -90° was monitored by epr.<sup>7</sup> The signal for di-*t*-butyl nitroxide was present before the ozonation but disappeared shortly after ozone was introduced. This indicates that the nitroxide is not a product of reaction of ozone with di-*t*-butylhydroxylamine.

(7) See technique described in accompanying paper.<sup>1</sup>

**Reaction of Di-*t*-butyl Nitroxide (III) with Hydrogen Chloride and Chlorine.**—A solution of 0.1 g of di-*t*-butyl nitroxide in 2.5 ml of chloroform was treated with gaseous hydrogen chloride at  $-65^{\circ}$ , after which the reaction mixture was taken out of the cooling bath. The color of the reaction mixture turned from red to green to blue. A qualitative glpc determination of products, as described for the ozonation experiments, showed isobutene, *t*-butyl chloride, and 2-methyl-2-nitrosopropane. Evaporation of the solution left a solid which was identified as di-*t*-butylhydroxylammonium chloride by its ir spectrum. Similar results were obtained upon similar treatment of di-*t*-butyl nitroxide with chlorine.

**Registry No.**—III, 2406-25-9; di-*t*-butylhydroxylamine, 10531-39-2; VI, 4432-73-9.

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## Addition of Dinitrogen Trioxide to Nonconjugated Dienes

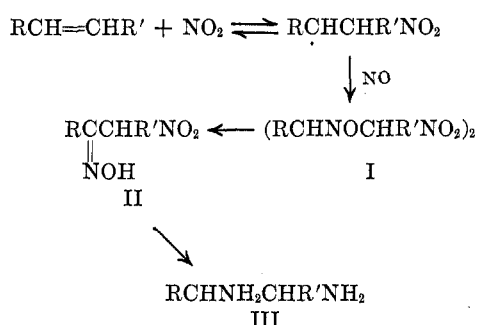
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The addition of dinitrogen trioxide is shown to proceed selectively at the bicyclic double bond of dicyclopentadiene. Simple adduct formation without transannular reaction occurs with 1,5-cyclooctadiene; however, norbornadiene undergoes considerable transannular addition to give nortricyclene derivatives. Reduction of the adducts leads to hydroxylamino oxime derivatives and diamines. The course of addition of nitrogen oxides is interpreted by a free-radical pathway.

The reaction of olefins with dinitrogen trioxide or with a mixture of nitrogen oxides to form 1:1 adducts is a classical technique of introducing two vicinal carbon-nitrogen bonds into an olefinic system.<sup>2a</sup> The adducts, known as pseudonitrosites, are usually 2-nitronitroso dimers I which can be thermally rearranged to the more soluble  $\alpha$ -nitroximes II, and subsequently reduced to vicinal diamines III. The addition of dinitrogen trioxide is believed to involve reversible attack of nitrogen dioxide on olefin with the formation of a free-radical intermediate containing a carbon-nitrogen bond which can combine with nitric oxide and dimerize, resulting in the adduct I.<sup>2b,c</sup>



It was of interest to determine whether the formation of these adducts from cyclic, nonconjugated dienes occurs selectively and whether transannular reactions take place. Dicyclopentadiene, 4-vinylcyclohexene-1, 1,5-cyclooctadiene, and norbornadiene were selected as cases for study. The results are in no disagreement with a free-radical mechanism and are interpreted accordingly.

**Dicyclopentadiene- $\text{N}_2\text{O}_3$ .**—Dicyclopentadiene was reported to form a pseudonitrosite in 1908;<sup>3</sup> however, the structure of dicyclopentadiene was unknown at

that time, and consequently the structure proposed for the adduct was incorrect. Examination of the nmr spectrum reveals that one double bond manifested as a singlet at  $\delta$  5.0 ppm (in  $\text{CDCl}_3$ ) is present. Cyclopentene exhibits a singlet at  $\delta$  5.7 ppm, whereas the bicyclic double bond in norbornene and in dicyclopentadiene is observed as an unsymmetrical triplet at  $\delta$  6.0 ppm. The singlet character and relative upfield position of the olefinic signal would suggest a cyclopentenyl rather than a norbornenyl double bond. Furthermore, the presence of a bicyclic double bond affects the chemical shift of the bridge protons; the 7s and 7a protons in norbornene and dicyclopentadiene show absorption patterns in the area of  $\delta$  1–1.5 ppm, whereas the spectrum of the pseudonitrosite possesses no signals in this region. A competition experiment involving a mixture of norbornene and cyclopentene with a limited quantity of nitrogen oxides results in almost exclusive consumption of the norbornene and formation of norbornene pseudonitrosite<sup>4</sup> rather than the cyclopentene derivative, indicating that a norbornenyl bicyclic double bond is intrinsically more reactive toward nitrogen oxides than is a cyclopentene system.

It is likely that the products are derived chiefly from *exo-cis* addition as in the case of norbornene,<sup>4</sup> but in this case there is less certainty. There are two *exo-cis* addition products for dicyclopentadiene IV and IVa, differing in the position of the double bond, and at least three types of dimers possible: dimers of IV and IVa, and the mixed dimer of IV and IVa, as well as *cis*- and *trans*-nitroso dimer forms, *i.e.*, geometric isomers *cis* and *trans* with respect to the nitrogen-nitrogen bond. Isomerization to the nitroxime affords a product whose nmr spectrum reveals a doublet of area 1 at  $\delta$  4.8 ppm, attributable to the highly shielded proton attached to the carbon atom bearing the nitro group. The 2-cps coupling reflected also in the signal assigned to the 7-*anti* bridge hydrogen at  $\delta$  1.8 ppm suggests that the 3 proton lies in an *endo* position, as in the case of norbornene nitroxime.<sup>4</sup> The nitroxime most likely

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